BNL-72029-2004-JA

AN OZONE EPISODE IN THE PHILADELPHIA METROPOLITAN AREA

Lawrence I. Kleinman[1], William F. Ryan[2], Peter H. Daum[1], Stephen R. Springston[1], Yin-Nan Lee[1], Linda J. Nunnermacker[1], and Judith Weinstein-Lloyd[3]

January 2004

Prepared for
Journal of Geophysical Researh

[1] Atmospheric Sciences Division, Brookhaven National Laboratory, Upton, NY 11973
[2] Department of Meteorology, The Pennsylvania State University, University Park, PA 16802
[3] Chemistry/Physics Department, SUNY/Old Westbury, Old Westbury, NY 11568

This research was performed under the auspices of the United States Department of Energy under Contract No. DE-AC02-76CH10886.

Abstract

In July and August of 1999, a Northeast Oxidant and Particle Study (NE-OPS) field campaign was conducted in the Philadelphia metropolitan area to determine causes for episodically high levels of O_3 and PM2.5, focusing on the coupling of chemical and meteorological processes. We report emission estimates, weather information, surface O_3 monitoring data, and aircraft observations, focusing on July 31, the last day of an O_3 episode in which concentrations in Philadelphia reached 165 ppb, the highest level observed there in the past 11 years. As is common in the northeastern states, this O_3 episode started with the development of a broad ridge over the central U.S. and ended with the Northeast Corridor under the influence of an Appalachian lee trough with air flow from the SW in an along-corridor direction. For a portion of the morning of July 31, winds were nearly stagnant allowing local emissions to accumulate. In contrast to typical O_3 episodes in the Northeast, transport on July 31 was limited and O_3 hot spots occurred close to NO_x and VOC emission sources. High O_3 was observed downwind of Baltimore and Philadelphia, both major urban areas. High O_3 was also observed in a less likely region near the Delaware – Pennsylvania border, downwind of Wilmington, DE but near utility and industrial emission sources. Surface O_3 monitoring data and morning aircraft observations show that the residual layer aloft contained 80 – 100 ppb of O_3, but almost no O_3 precursors. Same-day photochemistry on July 31 caused surface O_3 concentrations to increase by 60 – 80 ppb. Photochemical model calculations indicate O_3 production rates in excess of 20 ppb h^{-1}, in regions with NO_x > 5 ppb. High NO_x concentrations are a consequence of poor ventilation. Peroxide observations and calculations indicate that O_3 production is VOC limited in the high NO_x portions of the Philadelphia urban plume. Our results are contrasted against a severe O_3 episode that occurred in 1995, with possible emission control differences noted.

1. Introduction

Episodically high levels of O_3 are experienced several times each summer along the Northeast Corridor; a region on the East Coast of the U.S., stretching from Washington DC to Boston and including the Baltimore, Philadelphia, and NYC metropolitan areas. More than 40 million people live in this region. The Northeast Corridor is a region with high emission rates of the O_3 precursors, NO_x and VOCs. In addition to a vehicle dominated urban source, which more or less follows population density, there are locations within the corridor with a concentration of electric utilities, chemical plants, and oil refineries. To the west of the corridor, in central Pennsylvania and the Ohio River Valley, are large coal fired power plants with high emissions of SO_2 and NO_x. Meteorological conditions determine how these sources contribute to O_3 production.

In July and August of 1999, a Northeast Oxidant and Particle Study (NE-OPS) field campaign was conducted to determine causes for episodically high levels of O_3 and PM2.5, focusing on the coupling of chemical and meteorological processes. The study was centered around the Philadelphia metropolitan area with regional coverage supplied by aircraft flights. An overview of the program is given by *Philbrick et al.* [2002]. Major components of the field campaign included aircraft operated by the University of Maryland and the Department of Energy (DOE), enhanced surface and upper air meteorological observations, and instrumented surface sites located in central New Jersey [*Marley and Gaffney*, 2002] and at the Baxter Water Treatment Facility on the Delaware River, 18 km ENE from downtown Philadelphia. The Baxter site contained an extensive suite of aerosol [*Allen and Koutrakis*, 2002] and trace gas instrumentation [*Munger et al.*, 2002]. Lidar and balloon instruments [*Li et al.*, 2002] were used for probing the vertical structure and composition of the atmosphere.

Eight pollution episodes, with elevated concentrations of either O_3 or PM 2.5 or both, occurred within the 9 week field campaign [*Clark et al.*, 2002; *Ryan*, 2003]. This study focuses on the July 27-31 episode and in particular on the last day in which O_3 concentration at the Baxter site reached 165 ppb, the highest level observed in Philadelphia in the last 11 years

[*Clark et al.*, 2002]. The episode started with the development of a broad ridge over the central U.S. and ended with the Northeast Corridor under the influence of an Appalachian lee trough with air flow in the along-corridor direction. For a portion of the morning of July 31, winds were nearly stagnant allowing local emissions to accumulate. On the afternoon of July 31 there were high O_3 regions downwind of Baltimore and Philadelphia and near the DE –PA border. These regions were located in a narrow belt that paralleled the Delaware River and I-95 Interstate highway, which will be referred to as the "I-95 corridor".

Aircraft data are presented from 2 flights on July 31 which boxed the Philadelphia metropolitan area, encountering high O_3 plumes as the I-95 corridor was crossed to the northeast and southwest of the city. Wind observations and back trajectories indicate that these plumes draw upon a common regional background but, under the prevailing light wind conditions, have separate local emission inputs. Surface O_3 observations and vertical profiles from the DOE G-1 are used to address the question of how much O_3 is transported into the region in a residual layer aloft versus same-day O_3 chemically formed on the 31st. According to back trajectories and trace gas measurements from the G-1, the high O_3 area at the DE-PA border, southwest of Philadelphia, is downwind of Wilmington, DE and is influenced by nearby utility and/or industrial emission sources.

The 1999 NE-OPS field campaign was conducted in a region which had been intensively investigated by NARSTO-NE field campaigns conducted in 1995 and 1996. A severe O_3 episode occurred in mid-July of 1995 with violations of the 1 hour, 120 ppb, O_3 National Ambient Air Quality Standard (NAAQS) in a region between Washington DC and Maine. The episode lasted 4 days (July 12-15) with peak O_3 concentrations above 175 ppb for 2 days (July 14-15) [*Roberts et al.*, 1996]. The analysis of this episode has provided a conceptual model for a prevalent category of episode in the mid-Atlantic states [*Ryan et al.*, 1998; *Zhang et al.*, 1998; *Seaman and Michelson*, 2000]. In our discussion of the July 31, 1999 episode we will use the July 1995 case for comparison, ending with some thoughts on emission control strategies.

2. Experiment and Calculations

Between July 23 and August 11, 1999, the DOE G-1 aircraft conducted 20 flights in and around the Philadelphia metropolitan area. There were 3 flight patterns; "morning urban", "afternoon urban", and "regional". Figures 1 and 2 show aircraft ground tracks for the July 31 morning and afternoon urban patterns; the regional pattern is described by *Fast et al.* [2002]. There were 8 morning and 8 afternoon flights, with 6 days having both. There were minor differences from day to day, caused by weather or air traffic control. The primary sampling altitude was between 400 and 900 m. Within the region labeled "Urban Box" in Fig. 1, there was a combination of spirals and horizontal transects to determine the vertical distribution of pollutants between 300 and 2300 m in the morning and 400 and 2500 m in the afternoon. Figure 1 also identifies geographic locations and surface monitoring sites referred to in this study.

Trace gas measurements on the G-1 consisted of O_3, NO, NO_y, CO, speciated VOCs, SO_2, HCHO, H_2O_2, and organic peroxides. This instrument package is the same as previously used and the reader is referred to the literature for additional information (see *Lee et al*. [1998] for HCHO; *Weinstein-Lloyd et al*. [1998] for peroxides; *Rudolph* [1999] for VOCs and *Nunnermacker et al.* [1998] for the remaining trace gases). The NO_2 channel of the $NO/NO_2/NO_y$ detector was not operating for most of the program. In its place, NO_2 was calculated from NO, O_3, and UV irradiance using the photostationary state relations. We estimate an accuracy of ± 25% based on NO_x to NO_y ratios in fresh plumes being typically in the range of 75 to 110%. Also on the G-1 were aerosol instruments, including a PCASP for measuring the number concentration of accumulation mode particles (0.1 – 3 μm), and meteorological and position instruments, giving temperature, pressure, dew point, UV radiation, wind speed and direction, altitude, latitude, and longitude.

A constrained steady state (CSS) box model was used to calculate the production rate of O_3, $P(O_3)$, based on trace gas observations from the G-1. Model inputs include measured

values for the concentration of O_3, NO, CO, speciated VOCs, HCHO, H_2O_2, and organic peroxides; actinic flux as deduced from an Eppley radiometer; and the meteorological state parameters, temperature, pressure, and humidity. The number of calculations is limited by data availability, in particular the number of VOC determinations obtained from canister samples. Within the CSS model, observed species are held constant and the fast radical chemistry is solved to yield $P(O_3)$. Calculations, including ones for Philadelphia, have been described elsewhere in more detail [*Kleinman et al., 2002a*].

During the July 27-31 episode, the NE-OPS campaign had 2 radio acoustic sounding systems (RASS) giving vertically resolved winds at Centerton, NJ and at the Baxter water treatment site in northern Philadelphia (see Fig.1). Mixing height information was available from rawinsondes launched 5 times daily at the Baxter site.

Throughout this study we will use Eastern Standard Time (EST) equal to UTC – 5 hours to identify measurement periods. For synoptic weather maps, we will also indicate the UTC time.

3. Emissions

Emission estimates were available from 2 sources. The SMOKE model [*Houyoux et al.*, 2000] provides hourly values on a 4 by 4 km grid and the National Emission Inventory Database [*EPA*, 2003] gives yearly average values for counties and for point sources. Figure 2 shows NO_x emissions estimates from the SMOKE model for 13:00 EST, Saturday, July 31, 1999. Along with the afternoon flight track, we have included on this figure, the location of 3 surface O_3 monitoring sites that recorded peak values on the 31st above 150 ppb.

Figure 1 identifies counties along the I-95 corridor, bordering the Delaware River. Emissions for 6 of these counties are given in Table 1. As can be seen from Fig. 2, most of these emissions are occurring from areas that are close to the river. For wind flow in the along-corridor direction, from southwest to northeast, New Castle, DE and Delaware (county), PA are

upwind of Philadelphia. According to Table 1, these counties have, in total, NO_x and VOC emissions comparable to Philadelphia. High emission rates also occur to the northeast of Philadelphia which is downwind of the city in along-corridor flow. Thus, for this flow condition it would not be surprising to see O_3 hot spots all along this section of the I-95 corridor.

As a way of putting the Philadelphia area emissions into perspective, we have listed in Table 1 NO_x and VOC emissions for Davidson county, Tennessee. This county contains the city of Nashville which was a focus of SOS field campaigns in 1995 and 1999. Under stagnation conditions, such as observed in the O_3 episode of July 11-13, 1995, urban area emissions (without significant admixture from nearby power plants) yielded a local O_3 maximum of 145 ppb at the downtown Polk office building [*Kleinman et al.*, 1998; *Valente et al.*, 1998; *Daum et al*,, 2000a]. Table 1 shows that Davidson County has a population comparable to New Castle, DE and somewhat higher emissions. While we recognize the importance of quantifying background concentrations, emission density, and ventilation, it appears that there are several areas along the I-95 corridor, each with sufficient local emissions to yield high O_3 events.

Seven grid cells in Fig. 2 are colored black indicating that they have NO_x emission rates close to or above 10^4 tons y^{-1}. Table 2 provides information on these high emission rate regions. Emissions in all 7 grid cells have large contributions from point sources. That these regions differ from a typical urban area can be seen from the ratio of CO/NO_x and VOC/NO_x, which are much lower than typical urban values, about 10 and 2, respectively. Some of the high NO_x grid cells contain significant VOC point source emissions, most notably cell number 3, on the DE-PA border. In that cell the CO/NO_x ratio suggests that vehicles supply less than 10% of the NO_x emissions and by inference less than 10% of the VOC emissions, yet the VOC/NO_x ratio is close to a typical urban value. Even if the high NO_x grid cells don't have high VOC emissions they are located near areas that do, which is crucial to rapid O_3

production. A variety of industries contribute to the high NO_x emission rates including electric utilities, petroleum refineries, and chemical plants.

4. Results: July 27-31 O_3 Episode

The highest O_3 concentrations observed in the Philadelphia metropolitan area during the 1999 NE-OPS intensive occurred on July 31, the final day of an O_3 episode starting on July 27. In this section we present surface O_3 monitoring data, meteorological data and back trajectories, and trace gas and aerosol observations from the G-1 aircraft. We focus on high O_3 areas observed near the DE – PA border and north of Philadelphia for which we have aircraft observations in the morning and afternoon of July 31. Aircraft data from other days is used to provide a more representative picture of pollutant vertical distributions and background concentrations. A time sequence of events drawing upon data presented in this section is given in Section 5.1. A time-line for easy reference is given in Table 3. Additional information including weather maps, back trajectories, and regional O_3 distributions, for the July 27-31 episode as well as other episodes during the 1999 NE-OPS campaign, can be found in *Clark et al.*, [2002] and *Ryan* [2003].

4.1 O_3 Concentration

Figure 3 shows the maximum 1 hour average O_3 concentration observed at surface monitoring sites on July 31. With the exception of 2 sites in northern NJ and lower NY, violations of the 120 ppb NAAQS are confined to a narrow region along the I-95 corridor between Washington, DC and just north of Philadelphia. Leaving aside the same 2 stations, a comparison of Figs. 2 and 3 shows that a characteristic of this O_3 episode is that high concentrations are observed close to high emission rate regions.

The time development of the last day of the July 27-31 episode is shown in Fig. 4 which presents hourly average O_3 monitoring data along with boundary layer observations from the morning and afternoon G-1 flights. Surface ozone concentrations in Fig. 4 are an average over a one hour period which is identified by it's ending time (i.e. the first panel labeled 9:00 EST

has O_3 averaged from 8:00 – 9:00 EST). Nighttime O_3 concentrations (not shown) were 0 to 30 ppb. Between 9:00 and 10:00, there is a large increase in O_3. At this hour we expect the O_3 increase to be primarily due to entrainment, augmented by local production. By 10:00, there is an extended area in northeastern MD and DE with $O_3 > 80$ ppb; a maximum value of 105 ppb occurs at a site roughly mid-way between Baltimore and Philadelphia. Monitoring sites close to the centers of Baltimore and Philadelphia and a site at Chester, PA located just north of the DE-PA border, lag behind in the widespread O_3 increase as would be expected if high NO_x conditions prevailed at those locations. In the afternoon, O_3 maxima above 150 ppb were recorded at 4 monitoring sites: Aldino, MD, 48 km NE of Baltimore (154 ppb at 16:00); Chester, PA, near the DE-PA border (162 ppb at 14:00); Elmwood Street in Philadelphia (154 ppb at 14:00), and Bristol, PA, 29 km NE of Philadelphia (151 ppb at 15:00).

In anticipation of back trajectory results, presented below, indicating limited transport on the morning of July 31, we will refer to the area near the DE- PA border as the Delaware plume. The other 3 peak O_3 areas will be called the Baltimore, Philadelphia, and North Philadelphia plumes. A comparison from one hour to the next reveals only limited evidence of transport. In particular, there is no evidence that the Delaware plume is due to transport from Baltimore.

Areas of highest O_3 are clustered along the I-95 corridor, not coincidentally where most of the monitoring stations are located. Figure 2 shows that high NO_x emissions although occurring over much of the Philadelphia metropolitan area, are concentrated along the I-95 corridor, near the Delaware River, where large point sources are located. Figure 4, panels (e) and (f) show that the O_3 plumes observed from the G-1 peak close to I-95 and the Delaware River, with a drop off of several 10's of ppb, 10 km from the peak. Consistent with the narrowness of the O_3 plume observed from the G-1 are sharp spatial gradients observed from the surface monitoring network. For example, at the time that Chester, PA had an O_3 peak of 162 ppb, a monitoring station 16 km away recorded an O_3 concentrations of 108 ppb.

4.2 Meteorology

Weather conditions during the July 27-31 episode were hot and dry as typical of an extended drought that occurred in the mid-Atlantic region between mid-June and late August of 1999. The severe pollution event of July 31st occurred in the midst of a two-week heat wave with maximum temperatures exceeding 32 ^{o}C daily from July 23 through August 6.

The large-scale weather pattern early in the episode featured a broad ridge over the central U.S. (Fig. 5) with a weak trough exiting the Canadian Maritimes. This is a typical scenario for the onset phase of a high regional O_3 episode. The high pressure ridge leads to subsidence along the eastern tier of states, a lowering of the mixed layer height, generally clear skies, and warm air advection. All of these attributes promote O_3 formation. The usual progression as epitomized by the July 12-15, 1995 episode [*Ryan et al,* 1998] is for the ridge to expand eastward bringing warmer and more stable conditions with sustained west to northwest transport. In the July 1999 episode the upper air ridge axis remained nearly stationary through the early period of high regional O_3 (July 27-29). While O_3 concentrations were above average region wide from July 27-29, strong winds and intermittent convection, associated with meso-scale disturbances cresting the ridge and dropping down its eastern slope, prevented the development of extremely high concentrations. Late on July 30th, however, as the last in a series of disturbances moved offshore, the ridge quickly built eastward (Fig. 6) and O_3 concentrations increased dramatically in the mid-Atlantic region.

A weak surface pressure gradient over the mid-Atlantic evolves early on July 31 into an Appalachian lee side trough (ALT) that is characteristic of high O_3 episodes in the mid-Atlantic [*Pagnotti,* 1987; *Weisman,* 1990] and, more particularly, of the extreme episode of July 12-15, 1995 [*Seaman and Michelson,* 1998]. As the last disturbance moved south of Nantucket, MA at 0600 UTC (1:00 EST) on July 31, the lee side trough begins to develop and is analyzed at 1200 UTC (7:00 EST) along a line from southern NH through western CT and central NJ. The trough remains nearly stationary south of the Baltimore-Washington corridor but retrogrades westward during the day north of Baltimore (Fig. 7).

The structure and movement of the ALT has important implications for air chemistry in the mid-Atlantic region. As shown in *Pagnotti* [1987] , and later by *Seaman and Michelson* [1998], when the axis of the ALT is aligned with the belt of high emissions along the I-95 corridor, convergence of polluted air and enhanced O_3 production occur. In addition, mixing heights are reduced along and east of the trough axis so that the polluted air is trapped within a shallow layer leading to even higher concentrations [*Seaman and Michelson*, 1998]. Figures 4 and 7 show that on July 31, 1999 the ALT was aligned with the high-emission, high-O_3 I-95 corridor, as was the case also during the July 1995 episode.

On July 31, 1999, an additional factor, a short-lived cyclonic circulation embedded within the ALT, enhanced the potential for a local high O_3 event by introducing a period of stagnation and re-circulation of locally emitted pollutants. This circulation, was centered over the northern Chesapeake Bay at 0900 UTC (4:00 EST) according to Eta Data Assimilation System (EDAS) wind fields shown in Fig. 8. During the morning hours, the low moved slowly northward reaching Wilmington at 1500 UTC (10:00 EST). Wind speed remained low during the day, particularly on the west side of the I-95 corridor. The circulation persisted for about 10 hours becoming indistinct by 1800 UTC (13:00 EST) as southerly winds increased along the corridor.

Measurements from RASS units at Baxter and Centerton provide wind information in the NE-OPS region at altitudes pertinent to boundary layer pollutant transport. Figure 9 shows layer-averaged wind speed and direction at Baxter for a 30 hour period between 12:00 July 30 and 18:00 July 31. Starting at about 10:00 on July 31, winds measured from both RASS units were roughly from the SW, in the along-corridor direction. Wind speeds at Baxter were low, averaging 1-2 m s^{-1} from 18:00 on the 30th up until 1 hour before the last O_3 maximum at 16:00 on the 31st. During the early morning hours of the 31st both sites recorded periods of E or NE winds consistent with a cyclonic circulation located to the S or SE. Surface stations at PHL and Philadelphia Northeast Airport also observed a period of easterly winds consistent with a center

of circulation south of the Philadelphia metropolitan area. The EDAS wind fields show a pronounced cyclonic circulation extending from the surface to 600-700 m above ground level. Above that level, a weak trough is present.

4.3 Back trajectories

The combination of light winds, subsidence, vertical wind shear, and mesoscale circulation features make the determination of back trajectories problematic. Our calculations will be used only qualitatively to identify broad features of source regions. Two sets of back trajectories were calculated, one using the online Hybrid Single-Particle LaGrangian Integrated Trajectory (Hysplit) model [*Draxler and Rolph*, 2003; *Rolph*, 2003] and the other a vector addition of layer average winds observed from the Baxter RASS.

The Hysplit model with EDAS winds has a spatial resolution of approximately 40 km and is used here to illustrate larger scale features. Back trajectories shown in Fig. 10 terminate at a mid-boundary layer height of 1000 m at the times and locations where 3 of the 4 surface O_3 maxima were observed on July 31. Initially, the trajectories move fairly quickly in the persistent upper level northwesterly winds. As the trajectories subside during the morning hours of July 31, they change direction and speeds diminish as they come under the influence of the ALT. Finally, later in the day, the flow is directed along the I-95 corridor. Hysplit trajectories at altitudes, between 100 and 1500 m (not shown) also indicate an upwind source region to the northwest. Going back 1 to 2 days, the back trajectories reach Lake Erie, intercepting a region that, depending on altitude and termination point, includes Cleveland, OH and Buffalo, NY.

Constant altitude back trajectories calculated using vector average winds from the Baxter RASS with a termination time of 14:00 or 15:00 as appropriate for the O_3 maximum in the Delaware and North Philadelphia plumes, respectively, are shown in Fig. 11. Note that the Baxter RASS is located only 11 km from the North Philadelphia O_3 max and 41 km from the Delaware plume. Because wind speeds are low the 8 hour long back trajectories shown in Fig.

11 never get very far away from the Baxter RASS site. In the near surface layer (137-247 m) there is almost complete stagnation. At higher altitudes transport is in the along-corridor direction for several hours before maximum O_3, curving to the west – northwest – or north, depending on altitude, at earlier times. According to the RASS trajectories in Fig. 11, the O_3 monitoring sites are seen to draw upon pollutants coming from a limited distance but from a wide range in direction.

4.4 Morning Vertical Profiles

Measurements made at an altitude above the morning mixed layer are not affected by the current days surface emissions and therefore give an indication of the overnight transport of O_3 and its precursors. As the day develops, the convective mixed layer grows in height and pollutants from this residual layer will be entrained downwards and can influence surface air quality [*Berkowitz and Shaw*, 1997, *Ryan et al.*, 1998; *Zhang et al.*, 1998; *Berkowitz et al.*, 2000]. We examine the morning aircraft observations as a function of altitude to determine the general pattern of overnight transport and specific features of July 31.

A combination of vertical spirals and horizontal transects in the morning flights was used to determine the distribution of O_3 and other pollutants as a function of altitude. Vertical sampling was done at a location 20 km to the NE of downtown Philadelphia in the Urban Box shown in Fig. 1. This region contains a segment of the Delaware River, industrial facilities near the river, and a heavily traveled interstate highway. Data from 8 morning flights have been used to determine the frequency distribution of O_3, NO, SO_2, and PCASP. Results, averaged over 500 m altitude bins, are presented in Fig. 12. Two sets of frequency distributions are presented; one for July 31 and one for the other 7 morning flights. In general, observations between the surface and 500 m are in the morning mixed layer and those above 1000 m are in the residual layer from the day before. Measurements between 500 and 1000 m could be in the mixed or residual layer depending on time of day and day to day changes in boundary layer structure. In constructing Fig. 12 we have removed mixed layer observations at

attitudes above 500 m relying on a procedure developed by *Berkowitz and Shaw* [1997]. Results agree with rawinsonde temperature profiles where available.

The July 31 vertical profiles show that there is a layer between 500 and 1000 m altitude containing high concentrations of O_3, SO_2, aerosol particles, but not NO. Ozone and aerosol particles in this layer both stand out as being in significantly greater concentration than observed in any of the other 7 flights. Between 1000 and 2000 m, the July 31st concentrations approach the 7 flight average and at the highest altitude (> 2000 m) fall below that average. Within the surface to 1000 m layers, O_3 on July 31 varies between 48 and 101 ppb. The lowest concentrations occur near the surface and are caused by titration with 10's of ppb NO_x from I-95 interstate highway. On 2 horizontal transects at 725 and 900 m altitude, O_3 reaches 101 and 100 ppb, respectively, and varies by up to 25 ppb in a distance of less than 20 km. Over this distance SO_2 varies from 4 to 16 ppb, PCASP from 1700 to 3900 cm^{-3}, and NO from near 0 to 0.17 ppb. According to a rawinsonde taken within 30 minutes and 30 km of this data segment, this air mass is clearly above the top of the morning mixed layer ($\approx$ 400 m at 9:00). Because of the low NO concentration, calculated values of $P(O_3)$ are close to zero, so essentially all of the O_3 above 500 m is due to chemistry occurring on the previous day or days.

The occurrence of significant concentrations of SO_2, O_3, and aerosol particles but not NO, in the morning residual layer is a general feature of the 8 day data set. Apparently the short lifetime of NO_x due to OH chemistry in the daytime and NO_3/N_2O_5 chemistry at night does not allow it to survive overnight transport into our sampling region. SO_2, O_3, and aerosol particles, in contrast, have longer lifetimes.

4.5 Chemical Composition of the Delaware Plume

A persistent feature on most AM and PM flights were SO_2 and NO_x plumes encountered in a suburban/industrial area 30 km to the SW of downtown Philadelphia and 10 km NE of Wilmington, DE, near the Delaware River (see Fig. 1). High concentrations of CO, VOCs and aerosol particles were observed in the same area, but with less regularity. Industrial facilities

and a heavily traveled interstate highway (I-95) are underneath the flight track with additional point sources to the SW and NE of the flight track near the Delaware River.

Morning Flight

The Delaware plume was encountered at 9:49 at an altitude of 450 m. According to trace gas measurements on the G-1 and rawinsonde observations at 9:00 and 11:00 at Baxter, measurements are within the convective boundary layer which at this time is estimated to extend to 600 m. Wind speed as measured on the G-1 and by both RASS units was 1 m s^{-1} (Fig. 9).

Figure 13 shows the concentrations of trace gases and aerosol particles on the SW portion of the July 31 morning flight. The dominant feature in this figure is a plume, labeled "Industrial", located near the Delaware River with peak concentrations given by: SO_2 > 66 ppb, CO = 790 ppb, NO_y > 121ppb, NO = 110 ppb, and PCASP = 5480 cm^{-3}. Lower bounds are given for SO_2 and NO_y equal to the values where the data acquisition system went off-scale. Except for O_3, the concentrations of the trace gases shown in Fig. 13 were in each case the highest value recorded during the NE-OPS G-1 flights. The concentration of ethene (6.5 ppb), propene (4.9 ppb), and several other hydrocarbons were likewise the highest that we observed during the field campaign. Part of the plume traverse unfortunately coincided with an instrument zero period, accounting for the missing data in Fig. 13.

In addition to the intense primary plume, there is a 4 km wide plume, labeled "Ozone", that appears in Fig. 13 to be a shoulder next to the region with extremely high concentration spikes. Concentrations of NO_x, SO_2, and CO are high, but in contrast to the intense Industrial plume, there is a peak in O_3 and an even more pronounced peak in O_x. Properties of the O_3 plume are given in Table 4. Background values from a flight segment to the west of the industrial area are given in Table 4. For comparison we have determined concentrations observed in the same area on other days, an average of which is also given in Table 4. Although we are calling this region "background" we see from the average CO, SO_2, NO_x, and

NO_y that this region is by no means un-polluted. On the morning of July 31, O_3, HCHO, CO, and PCASP have particularly high concentrations.

Figure 13 shows that NO_x and NO_y are highly correlated but CO, NO_y, and SO_2 do not rise and fall in parallel. There are evidently multiple sources of these compounds encountered on the SW leg. The ratios calculated here are composite quantities that reflect the multiplicity of sources. NO_x to NO_y ratios shown in Table 4 indicate the presence of relatively un-aged emissions superimposed on an air mass with high concentrations of photochemical oxidation products including O_3, HCHO, NO_z, and aerosol particles. Because of high NO_x concentrations and the attendant titration, O_3 increases only moderately, from 85 ppb at the start of the plume to a peak value of 101 ppb. O_x, which is not affected by titration, increases from 89 to a peak value of 136 ppb.

It is clear from the extreme spatial gradients near the Delaware River and the high concentrations of reactive olefins that the plume in that location is from local industrial sources. However, we cannot tell if hydrocarbon concentrations are high because of high emission rates or because the sources are so close. Further away from the river, in the O_3 plume, several source types are possible contributors. The CO to NO_y ratio is consistent with an urban source while the SO_2 to NO_y ratio indicates an industrial and/or utility component.

Afternoon Flight

Trace gas concentrations from the July 31 afternoon flight are shown in Fig. 14. High O_3 concentration in the afternoon occurs in the same region in which high concentrations of primary pollutants were observed in the morning. Table 4 provides a summary of the afternoon plume and background measurements. In comparison to the morning observations, concentrations of primary pollutants are lower in the afternoon and the concentration of O_3 is significantly greater. The peak value of O_3 is 148 ppb, an increase of 63 ppb above the concentration in "background" air. O_x production efficiency is 3.9, almost the same as in the morning. A NO_x to NO_y ratio of 0.18 indicates significant photochemical aging. A comparison

between trace gas concentrations in Fig. 14 shows that O_3 is correlated with NO_y and SO_2 but less so with CO, implying an association with industrial emission sources.

A VOC sample was taken near the point of maximum O_3. In contrast to the morning sample, the afternoon sample does not have a high OH reactivity. The species profile in the afternoon resembles that found in most of the Philadelphia data set, which we take as a typical urban mixture due mainly to vehicular sources. Based on the VOC data and the other trace gas measurements, a $P(O_3)$ of 27 ppb h^{-1} is calculated. This is the 4th highest $P(O_3)$ out of 138 calculations done for the entire NE-OPS data set. Even though the NO_x to NO_y ratio indicates an aged air mass, the NO_x concentration is 6 ppb, which is nearly an optimum value for O_3 production given the observed VOC composition. Continued production of O_3 for the one hour that it took for this air mass to be advected to Chester, PA would more than account for the 162 ppb O_3 peak observed there.

4.6 Chemical Composition of North Philadelphia Plume

On the July 31 afternoon flight, the G-1 sampled in the North Philadelphia plume, upwind of Bristol, PA, where an O_3 peak of 151 ppb was observed later in the day. Three transects were made in the "Urban Box", two in the boundary layer and one at higher altitude. In addition a transect of the North Philadelphia plume was made just upwind of Bristol. Figure 4, panels (e) and (f) show O_3 concentrations in the North Philadelphia plume at an altitude of approximately 850 m. In both transects, and in an additional one at 450 m which is covered by the 850 m transect in panel (e), O_3 concentrations are seen to have a narrow peak near the west side of the Delaware River. We will focus on the 850 m crossing of the plume in the "Urban Box". This air takes 3 hours to be transported to Bristol, PA arriving there 2 hours after the surface O_3 maximum. Although the timing is off, observations from the afternoon transect in the "Urban Box" region should be reasonably representative of air masses that contribute to the surface O_3 maximum observed later in the afternoon.

Figure 2 (emissions) and Fig. 11 (back trajectories) show that the transects in the Urban Box are just upwind of a high emission rate region located near the west bank of the Delaware River. Trace gas observations are shown in Fig. 15. The narrow NO_x and SO_2 peaks, one of which coincides with a titration dip in O_3, appear to be due to nearby point sources. These peaks are superimposed upon a high background of NO_y, SO_2, and CO, which in the latter case is evidence for a traffic dominated urban source. Two CSS calculations, one on the 850 m transect and one on the 450 m transect, indicate rapid O_3 production ($P(O_3) > 20$ ppb h^{-1}) for NO_x concentrations greater than 5 ppb, a concentration that is exceeded in the central 10 km of the O_3 plume. Within the urban/industrial plume, total-peroxide decreases by 40%, similar to other urban plumes [*Jobson et al.,* 1998; *Weinstein-Lloyd et al.,* 1998; *Daum et al.,* 2003] and suggesting VOC limited O_3 production. The $P(O_3)$ calculations provide confirming evidence, showing that O_3 production is VOC limited for NO_x concentrations greater than about 5 ppb.

5. Discussion

The July 27-31, 1999 episode was unusual in that the peak O_3 concentrations observed on the 31st were due in large part to stagnation occurring on that morning. It is more usual in this region for O_3 episodes to occur under conditions that favor moderate transport along the Northeast Corridor [*Schichtel and Husar,* 2001]. In this section we summarize the events leading to the localized high O_3 peaks observed on the 31st (see also, Table 3). For comparison we describe the well-documented July 11- 15, 1995 episode which featured higher wind speeds and a more spatially extended area of high O_3. The comparison between the 1995 and 1999 episodes suggests some similarities and some differences in emission control strategies.

5.1. Summary of events leading up to July 31 O_3 maxima

Based on back trajectories, surface O_3 observations, residual layer measurements, and G-1 intercepts of the Delaware and North Philadelphia plumes we can construct a chain of events leading to the 162 ppb O_3 maximum observed at Chester, PA (Delaware plume) at 14:00 and the 151 ppb O_3 maximum observed in at Bristol, PA (North Philadelphia plume) at 15:00 on July 31. Hysplit back trajectories (Fig. 10) indicate that the air mass was transported to the

mid-Atlantic region from the northwest in the vicinity of Cleveland, OH and Buffalo, NY. It subsequently passed over central PA, arriving near the I-95 corridor on the morning of July 31. Hysplit back trajectories calculated by *Ryan et al.* [1998] for the 12 most severe O_3 episodes in the Baltimore – Washington area during 1995-1996 indicate transport mainly from the west or northwest with a variability that would include the July 31, 1999 case. Most of the trajectories calculated by *Ryan et al.* [1998] pass over the Ohio River Valley, but some, like the July 1999 case evidently receive their pollutants from other locations.

Morning aircraft measurements in the nighttime residual layer indicate that this air mass has, in places, an O_3 concentration up to 100 ppb as well as high levels of NO_y, SO_2, and accumulation mode aerosol particles; the latter 2 substances indicating utility emissions. SO_2 is not responsible for O_3 formation but co-emitted NO_x added to hydrocarbons from man-made or biogenic sources is. The concentration of O_3 precursors, NO_x and reactive hydrocarbons, is low so the formation of additional O_3 depends on local emissions, as observed elsewhere [*Berkowitz et al.*, 2000]. Downward mixing of this air mass by the growing convective boundary layer, results in high surface O_3 concentrations. At 10:00 an O_3 concentration of 105 ppb is recorded at Lums, DE. Monitoring sites north of the DE border generally did not have a similarly rapid morning rise in O_3, possibly due to titration in this high emission rate region. Low altitude morning observations by the G-1 in the "Urban Box" indicate areas in which several tens of ppb of O_3 have been titrated by NO.

In the morning and early afternoon local emissions are added to the imported pollutants. Because of light winds in the vicinity of the ALT, as indicated by both the Hysplit trajectories and RASS winds, and the turning associated with the embedded circulation, air parcels have a long residence time over the I-95 corridor (see Figs. 10-11). In the several hours before peak O_3 levels are observed, transport is mainly from the SW in an along-corridor direction. Although the precise locations of local emission sources cannot be determined because of wind shear and trajectory uncertainties, it is clear that with wind speeds of 1-2 m s^{-1}, the O_3 maxima each have their own local source regions. Aircraft measurements in the plumes, upwind of the

surface O_3 maxima indicate a complex mixture of urban, utility, and industrial emissions. The emission sources shown in Fig. 2 as well as the observation of very high concentrations of reactive olefins lead us to believe that chemical plants or refineries are important to O_3 formation in the Delaware plume. SO_2 concentrations of several 10's of ppb in both the Delaware and North Philadelphia plume point towards a utility or industrial component while CO concentrations above 375 ppb in both plumes indicate an urban component.

Judging from the morning aircraft samples in the residual layer and from the 10:00 surface O_3 observations, photochemistry on the 31st starts out with 80 – 100 ppb O_3 from the previous day. An additional 60 – 80 ppb must be formed on the 31st to account for the observed surface O_3 maxima. Early afternoon O_3 production rate in parts of the Delaware and North Philadelphia plumes are greater than 20 ppb h^{-1}, which if sustained through a several hour period could account for the observed peaks. A key factor to achieving such rates is the availability of NO_x, which in the high $P(O_3)$ samples was greater than 5 ppb. Maintaining this NO_x level depends on transport along a high emission rate region such as the I-95 corridor.

5.2 Comparison with July 1995 Episode

The mid –July 1995 O_3 episode in which NAAQS exceedances were recorded over the Northeast Corridor between Washington DC and Maine was exceptionally well documented and is thought to be representative of a class of conditions that are responsible for many of the sustained high O_3 cases. Meteorological conditions leading to the 1995 and 1999 episodes were similar, although the 1995 event featured a more robust and northward extending upper air ridge that led to a number of boundary layer effects causing more sustained and widespread high O_3. In each case, the geographic distribution of high O_3 follows the location and development of the Appalachian lee side trough.

Meteorological conditions

Both the 1995 and 1999 episodes began with an upper level ridge over the central U.S. In 1995 the ridge moved steadily east-northeast with its center moving from northwestern

Oklahoma on July 11 (Fig. 16) to Indiana by July 14 (Fig. 17). In 1999, in contrast, the ridge nosed northeastward only belatedly late on July 30. A comparison between Figs. 5 and 16 shows that the upper air ridge at the onset of the 1995 episode is stronger and extends further north than in the 1999 event. Near the peak of the episodes, a comparison of Figs. 8 and 17 shows that height gradients in the mid-Atlantic region, associated with the ridge were weaker in 1995.

As a consequence of the ridge positions and height gradients, boundary layer ventilation was reduced in 1995 relative to 1999 (except for July 31) and winds were more westerly as indicated in Table 5. With the ridge located further north in 1995, convection over the mid-Atlantic was strongly suppressed, whereas in 1999, intermittent convection moderated the buildup of O_3. In conjunction with the upper level ridge building east during the 1995 episode, the boundary layer is characterized by the westward extension of the Bermuda High at lower levels (see Fig. 2 of *Ryan et al*, [1998]). The 1999 episode had a more persistent trough over New England which did not allow the Bermuda High to build west.

Weaker height gradients during the latter stages of the 1995 episode encouraged the development of mesoscale features that are weaker, or not present, during the 1999 episode. During the heart of the July 12-15 episode, on July 13 and 14, supplemental radiosonde observations identified a nocturnal low level jet (LLJ) along the coastal plain at approximately 160-670 m agl with peak winds of 11-16 ms^{-1} [*Ryan et al.*, 1998]. The coastal LLJ is frequently observed during high O_3 periods due to the weak synoptic scale forcing usually associated with pollution events [*Ray et al.*, 1998; *Clark et al.*, 2002]. The nocturnal LLJ may be a key mechanism by which pollutants are transported along the mid-Atlantic corridor into New England [*Ray et al.*, 1998; *Seaman and Michelson*, 2000]. In the 1995 episode, O_3 concentrations in excess of the NAAQS were observed from North Carolina to New England [*Zhang et al.*, 1998; *Seaman and Michelson*, 2000]. In contrast, in 1999, stronger synoptic scale forcing resulted in more sustained northwesterly winds and suppressed the development

of the LLJ. This, in turn, limited the northward extent of the region of severe O_3 and a decrease in intra-regional transport [*Ryan*, 2003].

Imported O_3

The analysis of the 1995 episode clearly showed the importance of a pool of O_3 in the residual layer which when mixed down to the surface contributes to O_3 maxima later in the day. This conclusion was based on direct observations in the residual layer during early morning aircraft flights [*Ryan et al.*, 1998; *Zhang et al.*, 1998], surface O_3 time trends, and photochemical modeling studies [*Zhang et al.*, 1998]. It was estimated that an air mass that reached peak O_3 concentrations of 150 – 185 ppb started the day with 80 – 100 ppb of O_3. We reach a similar conclusion for the 1999 episode based on morning aircraft observations NE of Philadelphia and based on the morning surface O_3 observations. As the other 7 morning flights show, afternoons without high surface O_3 tend to have started out with lower levels of O_3 in the morning residual layer.

O_3 distribution and transport distance

For most of the 1999 episode, horizontal ventilation was greater than in 1995. However the last day of the 1999 episode had a very different character. On July 31, boundary layer winds near the I-95 corridor, under the influence of a retrograding ALT and embedded cyclonic circulation, became nearly stagnant, allowing for the accumulation of O_3 from relatively nearby emission sources (see Fig. 11). Wind speeds at 500 m on the morning of July 31, 1999 were 1-2 m s^{-1}. whereas on the mornings of July 14-15. 1995, they were 5-7 m s^{-1}. The 1995 case is the more typical one, in that O_3 episodes in the Northeast U.S. tend to occur under conditions favoring transport, which accounts for such features as O_3 maxima in central CT and coastal Maine, more than 150 km downwind of NYC and Boston, respectively [*Schichtel and Husar*, 2001]. Differences in transport between 1995 and 1999 are manifested in the spatial distribution of O_3. In 1999, high O_3 is confined to a narrow region that follows the I-95 corridor (Fig. 3). Ozone maxima from the Philadelphia plume occur within 30 km of the city center. In 1995, in contrast, the region of high O_3 extended eastward 100 km into central NJ

[*Roberts et al.*, 1996; *Seaman and Michelson*, 2000 (Fig.1)]. Further evidence for the local nature of the O_3 episode on July 31 (compared with other 1999 events) is found in a series of regional scale transport/chemistry calculations done by *Fast et al.*, [2002].

Emission control implications

Although emission control strategies are best formulated using chemical transport models, our comparison between the 1995 and 1999 episodes qualitatively suggests some similarities and some differences in control measures. Both episodes depend on imported O_3, and both require control of upwind O_3 sources. Our observations indicate a utility component which we expect was important also in 1995 given the locations of back trajectories. Under conditions of moderate ventilation such as in the 1995 episode, transport will mix together emissions from across the metropolitan area, leading to a merged plume characteristic of an average emission mixture. Under the stagnation conditions of 1999, O_3 production draws upon local emissions which do not necessarily resemble the average. Emission control measures optimized for an entire metropolitan area with high vehicle emissions may not be optimum for a region such as the DE-PA border which, under light wind conditions, is impacted by local industrial and utility sources. Also, if reduced ventilation leads to higher concentrations of O_3 precursors, we expect, as a general rule, that O_3 production will shift towards more VOC limited conditions [*Sillman*, 1999; *Kleinman et al.*, 2001].

6. Conclusions

July 31, 1999 was the last day of an episode in which very high O_3 concentrations were observed in a narrow belt along the I-95 corridor from Washington, DC to north of Philadelphia. A distinctive feature of this episode was that wind speeds on the morning of the 31st were calm allowing local emissions to accumulate. In contrast to the well-studied episode on July 12-15, 1995, the highest O_3 concentrations occurred on a day with little transport. As a consequence O_3 hot spots, with 1 hour average concentrations up to 162 ppb, were located close to the emission areas that supplied the O_3 precursors.

Using surface O_3 observations, aircraft trace gas measurements, and synoptic weather information augmented by local soundings, we are able to determine causes for the high O_3 event on July 31. As in the 1995 case, inter-regional transport (in 1999 from the Northwest) brings to the Mid-Atlantic state air masses that contain up to 100 ppb O_3. Aircraft observations in the residual layer show that this air mass, while containing high concentrations of oxidation products such as O_3, NO_y, HCHO, and aerosol particles, contains very low concentrations of NO_x and VOCs. All further increases in O_3 concentration are due to local emissions.

The key events that turned July 31 into a day with very high O_3, were 1) the formation of an Appalachian lee trough directing air flow along high emission rate portions of the I-95 corridor and 2) the occurrence of a meso-scale low pressure feature over Chesapeake Bay which led to local stagnation and recirculation of pollutants. Ozone hot spots were located downwind of Baltimore, north of the DE- PA border, within Philadelphia, and north of Philadelphia. These areas drew upon a common high regional background put there by fumigation from a polluted residual layer. Sixty to 80 ppb O_3 needed to be formed on the morning and early afternoon of the 31st to account for the peak 1-hour average surface O_3 observations.

Aircraft observations in the Delaware plume and North Philadelphia plume indicate high concentrations of O_3 precursors that could support O_3 production rates in excess of 20 ppb h^{-1}. Calculations show that the O_3 production rate in areas where NO_x is greater than 5 ppb is VOC limited. The chemical composition of the precursors indicate a utility/industrial component added to an urban background.

Given the density of emission sources in the Baltimore and Philadelphia urban areas, it is not surprising that high O_3 concentration would occur downwind of these cities under conditions of light winds, approaching stagnation. The surprising feature of the regional O_3 distribution is that the highest 1-hour average surface concentration occurs in the "Delaware plume" just north of the DE – PA border. Evidently emissions from the Wilmington

metropolitan, augmented by local utilities, chemical plants, and refineries can, under near-stagnations condition, cause very high O_3 levels. Furthermore, a multi-day stagnation period is not required to accumulate sufficient precursors to form 60 – 80 ppb of O_3; 1/2 day or less is all that is needed. An emission control strategy formulated for the more common 1995 type episode may not be adequate to eliminate exceedances of the 1 h O_3 standard under the near stagnation conditions encountered on July 31, 1999.

Acknowledgements

We thank pilot Bob Hannigan and flight crew from PNNL for a job well done. We gratefully acknowledge the many contributions of John Hubbe of PNNL in collecting and reducing the data. A special thanks to Jerome Fast of PNNL for providing O_3 monitoring and emissions data. We thank Jochen Rudolph of York University for the analysis of hydrocarbon canisters. Weather and ozone climatology discussions with Carl Berkowitz of PNNL and Rich Clark of Millersville University were valuable. The many contributions of Russell Philbrick of Pennsylvania State University and others within the NE-OPs community are appreciated. The authors gratefully acknowledge the NOAA Air Resources Laboratory for the provision of the HYSPLIT transport and dispersion model and READY website used in this study. NE-OPS was funded through a grant (R826373) from the U.S. EPA. We acknowledge the support of the Atmospheric Chemistry Program within the Office of Biological and Environmental Research of DOE for providing the G-1 aircraft. This research was performed under sponsorship of the U.S DOE under contracts DE-AC02-76CH1088.

Table 1. Annual average NO_x and VOC emissions by county.

Location[a]	Population (1000's)	NO_x (k ton/year)		VOC (k ton/year)	
		Point	Total	Point	Total
West of Delaware River					
New Castle, DE	500	15	38	6	28
Delaware, PA	551	11	30	2	21
Philadelphia, PA	1518	6	56	3	56
East of Delaware River					
Salem, NJ	64	2	5	10	17
Gloucester, NJ	255	7	25	12	25
Camden, NJ	509	0.4	21	2	23
6 county total	3397	41	175	35	170
Davidson, TN	541	6	44	3	44

[a] See Fig. 1 for locations. Emissions data for 6 counties near Philadelphia for1999, Davidson County emissions for 1995 [*EPA*, 2003].

Table 2. Characteristics of high NO_x emission rate grid cells

No.[a]	Location	Type[b]	Emissions[c]		
			NO_x(kton y^{-1})	CO/NO_x	VOC/NO_x
1	Delaware City, DE	petroleum ref.	8785	0.9	0.4
2	Wilmington, DE	electric utility	14,132	2.7	0.5
3	DE-PA border	petroleum ref. chemical	9529	0.9	1.9
4	Gloucester Co., NJ	petroleum ref. chemical	12,233	0.8	0.1
5	Philadelphia, PA	petroleum ref.	29,787	3.3	0.9
6	Burlington Co., NJ	electric utility	10,232	0.6	0.2
7	Mercer Co., NJ	electric utility	13,899	0.7	0.3

[a] See Fig. 1 for locations.

[b] Sources identified from *EPA* [2003]. Only largest contributors listed.

[c] Emission estimates from SMOKE model [*Houyoux et al.*, 2000]. Ratios are moles to moles.

Table 3. Timeline of events in the July 27-31, 1999 O_3 episode.

Date	Time (EST)	Meteorology	Transport/Chemistry
7/27		Broad ridge over central U.S.	Moderate elevation of O_3 in Mid-Atlantic
7/27-30		Mesoscale disturbances cresting ridge and dropping down its eastern slope	O_3 limited by strong winds and convective venting
7/29-30			Transport from NW. Possible source regions near Cleveland, Buffalo, and central PA
7/30	19:00	Ridge builds eastward, weak surface pressure gradient in Mid-Atlantic	Residual layer forms. Observations 14 h later on the 31st show up to 100 ppb O_3, but low NO_x and VOCs. SO_2 and PM indicate utility source.
7/31	1:00	Appalachian lee trough begins to develop	Transport starts changing from NW to SW, along the I-95 corridor
7/31	4:00-10:00	Meso-scale low centered over N. Chesapeake Bay moves N to Wilmington	Stagnation and re-circulation of local emissions
7/31	10:00	Development of convective boundary layer	Entrainment of O_3 from residual layer leads to surface O_3 80-105 ppb
7/31	8:00-12:00	Stagnation near surface, low wind speed from W-SW below 1 km	NO_x and VOCs from high emission rate regions along I-95 corridor accumulate and are mixed with O_3 from aloft. Plume species indicate urban, utility and industrial inputs.
7/31	13:00	Local meso-low indistinct, wind speed increases	Transport aligned with high emission regions on I-95 corridor
7/31	10:00-14:00		$P(O_3) > 20$ ppb h^{-1} in high NO_x (>5 ppb) areas. O_3 accumulates
7/31	14:00-16:00	Increased wind speed in along-corridor direction	Surface O_3 maxima > 150 ppb near high emission rate regions

Table 4. Trace gas concentrations and ratios observed from the G-1 at ~ 500m altitude, in and near the Delaware plume on July 31 with a comparison to background observations from 7 other morning flights.

Quantity	7 AM flights	7/31 AM[a]		7/31 PM[b]	
	Background	Back.	O_3 Plume	Back.	Plume
Width (km)	14	14	4	8	11
O_3 (ppb)	52	78	91	85	142
O_x (ppb)	58	79	117	86	146
NO_x (ppb)	8.7	2.8	31	1.0	4.6
NO_y (ppb)	15	16	55	15	33
CO (ppb)	226	338	693	236	397
SO_2 (ppb)	5.6	8.7	25	7.5	26
HCHO (ppb)	2.3	4.7	7.0	3.5	5.0
PCASP (cm^{-3})	1575	3068	4320	2854	4734
O_x/NO_z			3.5[c]		3.9[d]
NO_x/NO_y		0.80[d]	0.77[d]		0.18[c]
SO_2/NO_y			0.42[c]		1.05[d]
CO/NO_y			9.1[c]		10.5[c]

[a] 7/31 AM data from 9:44 – 9:50 at 440 m.

[b] 7/31 PM data from 13:12 – 13:17 at 580 m.

[c] Low correlation. Ratio from Δ's i.e., $O_x/NO_z = (O_x(\text{plume}) - O_x(\text{background})) / (NO_z(\text{plume}) - NO_z(\text{background}))$

[d] slope from linear least squares regression, $r^2 > 0.85$.

Table 5. Comparison of boundary layer winds[1] for July 11-15, 1995 and July 27-31, 1999.

Year	Pressure (mb)	Speed ($m\ s^{-1}$)	Direction (°)
1995	950	4.2	258
1995	850	4.4	265
1999	950	5.6	320
1999	850	7.6	312

[1] Vector mean winds from Dulles International Airport, the closest National Weather Service sounding station to Philadelphia.

References

Allen, G.A., and P. Koutrakis, Relationships among surface observations of particle mass, number, composition, and gaseous precursors during the summer 1999 Philadelphia NE-OPS study, *4th Conf. on Atmos. Chem.,* preprint vol. pp 133-134, Amer. Meteor. Soc., Orlando, FL, Jan., 2002.

Berkowitz, C. M., and W. J. Shaw, Airborne measurements of boundary-layer chemistry during the SOS: A case study, J. Geophys. Res. 102(D11):12,795-12,804, 1997.

Berkowitz, C.M., J.D. Fast, and R.C. Easter, Boundary layer vertical exchange processes and the mass budget of ozone: Observations and model results, *J. Geophys. Res., 105,* 14,789-14,805, 2000.

Clark, R.D., C.R. Philbrick, W.F. Ryan, B.G. Doddridge, and J.W. Stehr, The effects of local and regional scale circulations on air pollutants during NARSTO-NE-OPS 1999-2001, *4th Conf. on Atmos. Chem.*, preprint vol. pp 125-132, Amer. Meteor. Soc., Orlando, FL, Jan., 2002.

Daum, P.H., L. Kleinman, D. Imre, L.J. Nunnermacker, Y.-N. Lee, S.R. Springston, L. Newman, J. Weinstein-Lloyd, R.J. Valente, R.E. Imhoff, R.L. Tanner, and J.F. Meagher, Analysis of O_3 formation during a stagnation episode in central Tennessee in summer 1995, *J. Geophys. Res., 105,* 9107-9119, 2000a.

Daum, P.H., L. Kleinman, D.G. Imre, L.J. Nunnermacker, Y.-N. Lee, S.R. Springston, L. Newman, and J. Weinstein-Lloyd, Analysis of the processing of Nashville urban emissions on July 3 and July 18, 1995, *J. Geophys. Res., 105*, 9155-9164, 2000b.

Daum, P.H., L.I. Kleinman, S.R. Springston, L.J. Nunnermacker, Y.-N. Lee, J. Weinstein-Lloyd, J. Zheng, and C. Berkowitz, A comparative study of O_3 formation in the Houston urban and industrial plumes during the TEXAQS 2000 Study. *J. Geophys. Res.,108* (D23), 4715, doi:10.1029/2003JD003552, 2003.

Draxler, R.R. and G.D. Rolph, HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website

(http://www.arl.noaa.gov/ready/hysplit4.html). NOAA Air Resources Laboratory, Silver Spring, MD, 2003.

EPA, National Emission Inventory (NEI) Database accessible from www.epa.gov/air/data/, 2003.

Fast, J.D., R. Zaveri, X. Bian, E.G. Chapman, and R.C. Easter, The effect of regional-scale transport on oxidants in the vicinity of Philadelphia during the 1999 NE-OPS field campaign, *J. Geophys. Res.*, *107* (D16), 4330, doi:10.1029/2001JD000980, 2002.

Houyoux, M., J. Vukovich, and J.E. Brandmeyer, Sparse Matrix Operator Kernel Emissions Modeling System, SMOKE User's Manual, MCNC-North Carolina Supercomputing Center, Environmental Programs, Research Triangle Park, NC. 2000.

Jobson, B.T., G.J. Frost, S. McKeen, T.B. Ryerson, M.P. Buhr, D.D. Parrish, M. Trainer, F.C. Fehsenfeld, Hydrogen peroxide dry deposition lifetime determined from observed loss rates in a power plant plume. *J. Geophys. Res.*, *103*, 22617-22628, 1998.

Kleinman, L.I., P.H. Daum, D.G. Imre, C. Cardelino, K.J. Olszyna, and R.G. Zika, Trace gas concentrations and emissions in downtown Nashville during the 1995 SOS/Nashville Intensive, *J. Geophys. Res.*, *103*, 22,545-22,553, 1998.

Kleinman, L.I., P.H. Daum, Y.-N. Lee, L.J. Nunnermacker, S.R. Springston, J. Weinstein-Lloyd, and J. Rudolph, Sensitivity of ozone production rate to ozone precursors. *Geophys. Res. Lett. 28*, 2903-2906, 2001.

Kleinman, L.I., P.H. Daum, D. Imre, Y.-N. Lee, L.J. Nunnermacker, S.R. Springston, J. Weinstein-Lloyd, and J. Rudolph, Ozone production rate and hydrocarbon reactivity in 5 urban areas: A cause of high ozone concentration in Houston, *Geophys. Res. Lett.*, *29*(10), 1467, doi:10.1029/2001GL014569, 2002a.

Kleinman, L.I., P.H. Daum, Y.-N. Lee, L.J. Nunnermacker, S.R. Springston, J. Weinstein-Lloyd, and J. Rudolph, Ozone Production Efficiency in an Urban Area, *J. Geophys. Res.*,*107*(23), 4733, doi:10.1029/2002JD002529, 2002b.

Lee Y.-N. et al., Atmospheric chemistry and distribution of formaldehyde and several multioxygenated compounds during the 1995 Nashville/Middle Tennessee Ozone Study, *J. Geophys. Res. 103*, 22,449-22,462, 1998.

Li, G., C.R. Philbrick, and G. Allen, Raman Lidar measurements of airborne particular matter, *4th Conf. on Atmos. Chem.*, preprint vol. pp 135-139, Amer. Meteor. Soc., Orlando, FL, Jan., 2002.

Marley, N.A., and J.S. Gaffney, Northeast Oxidant and Particle Study (NEOPS): Preliminary results from the Centerton, New Jersey, field site, *4th Conf. on Atmos. Chem.*, preprint vol. pp 115-120, Amer. Meteor. Soc., Orlando, FL, Jan., 2002.

Munger, J.W., B. Doddridge, and R. Clark, Interpretation of NO_y, O_3 and CO data from the Northeast Oxidant and Particle Study, *4th Conf. on Atmos. Chem.*, preprint vol. pp 153-156, Amer. Meteor. Soc., Orlando, FL, Jan., 2002.

Nunnermacker, L.J., D. Imre, P.H. Daum, L. Kleinman, Y.-N. Lee, J.H. Lee, S.R. Springston, L. Newman, J. Weinstein-Lloyd, W.T. Luke, R. Banta, R. Alvarez, C. Senff, S. Sillman, M. Holdren, G.W. Keigley, and X. Zhou, Characterization of the Nashville urban plume on July 3 and July 18, 1995, *J. Geophys., Res. 103*, 28,129-28,148, 1998.

Philbrick, C.R., et al., Overview of the NARSTO-NE-OPS program, *4th Conf. on Atmos. Chem.*, preprint vol. pp 107-114, Amer. Meteor. Soc., Orlando, FL, Jan., 2002.

Roberts, P.T., M.E. Korc, D.L. Blumenthal, and. P.K. Mueller, NARSTO-Northeast 1995 Summer Ozone Study, version 1.2, 94pp, EPRI, Palo Alto, CA, 1996.

Rolph, G.D., Real-time Environmental Applications and Display sYstem (READY), Website (http://www.arl.noaa.gov/ready/hysplit4.html).NOAA Air Resources Laboratory, Silver Spring, MD, 2003.

Rudolph, J., Measurement of Nonmethane hydrocarbons in the atmosphere, in R. Koppmann, and D. H. Ehhalt, (eds.), Volatile organic compounds in the Troposphere, Proceedings of the

Workshop on Volatile Organic Compounds in the Troposphere, Juelich (Germany) October 27-31, 1997, *Schriftenreihe des Forschungszentrum Jülich, 16*, 11-35, 1999.

Ryan, W.F., B.G. Doddridge, R.R. Dickerson, R.M. Morales, K.A. Hallock, P.T. Roberts, D.L. Blumenthal, J.A. Anderson, and K.L. Civerolo, Pollutant transport during a regional O_3 episode in the Mid-Atlantic states, *J. Air & Waste Manage. Assoc., 48*, 786-797, 1998.

Ryan, W.F., Discussion of the 1999 Ozone Season, www.atmos.umd.edu/~ryan/summary99.htm, 2003.

Schichtel, B.A. and R.B. Husar, Eastern North American transport climatology during high- and low-ozone days, *Atmos. Environ., 35*, 1029-1038, 2001.

Seaman, N.L., and S.A. Michelson, Microscale meteorological structure of a high-ozone episode during the 1995 NARSTO-Northeast Study, J. *Appl. Met., 39*, 384-398, 2000.

Sillman, S., The relation between ozone, NO_x, and hydrocarbons in urban and polluted rural environments, *Atmos. Environ., 33*, 1821-1845, 1999.

Valente, R.J., R.E. Imhoff, R.L. Tanner, J.F. Meagher, P.H. Daum, R.M. Hardesty, R.M. Banta, R.J. Alvarez, R.T. McNider, and N.V. Gillani, Ozone production during an air stagnation episode over Nashville, Tennessee, *J. Geophys. Res., 103*, 22,555-22,568, 1998.

Weinstein-Lloyd, J.B., J.H. Lee, P.H. Daum, L.I. Kleinman, L.J. Nunnermacker, S.R. Springston, and L. Newman, Measurements of peroxides and related species during the 1995 summer intensive of the Southern Oxidants Study in Nashville, Tennessee, *J. Geophys. Res., 103*, 22,361-22,373, 1998.

Weisman, R.A., An observational study of warm season southern Appalachian lee troughs. Part I: Boundary layer circulation, *Mon. Wea. Rev.*, 118, 950-962, 1990.

Zhang, J., S.T. Rao, and S.M. Daggupaty, Meteorological processes and ozone exceedances in the Northeastern United States during the 12-16 July 1995 episode, *J. Appl. Met., 37*, 776-789, 1998.

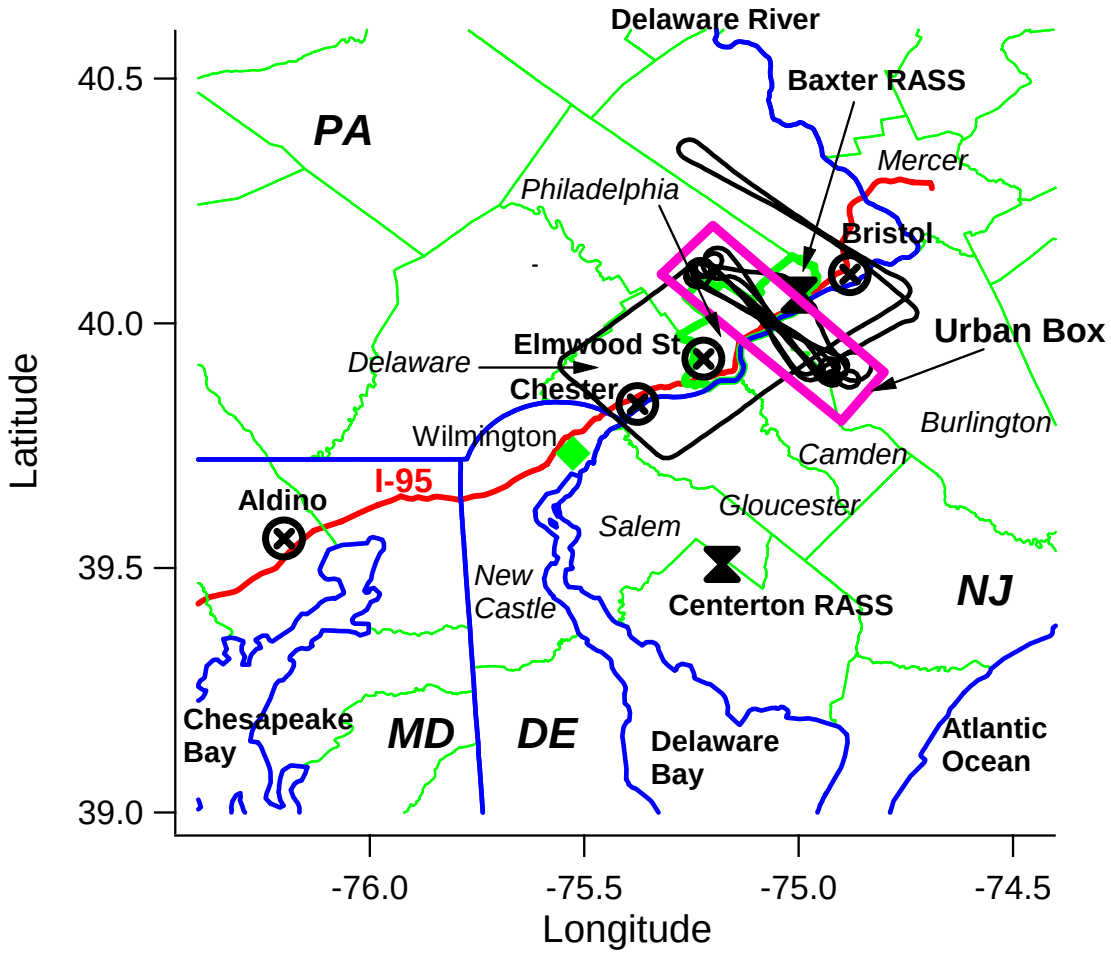

Figure 1. Map of experimental area showing the ground track for the July 31 morning G-1 flight. The rectangular area labeled "Urban Box" encloses a region in which there were vertical profiles and horizontal transects at altitudes between 300 and 2500 m. Location of RASS units at the Baxter Water Treatment Facility and in Centerton, NJ are noted. Circles with crosses indicate the 4 surface monitoring sites which recorded O_3 concentrations above 150 ppb on July 31, 1999. Geographic locations referred to in the text are identified as is I-95 Interstate highway.

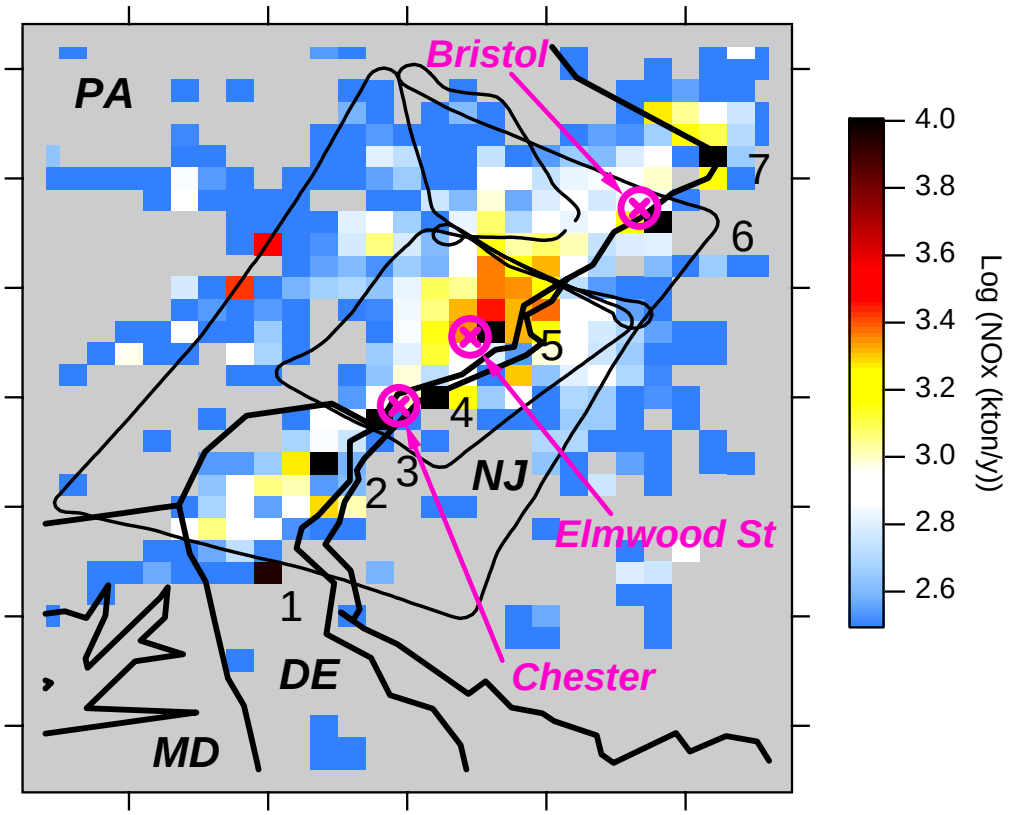

Figure 2. Map of Philadelphia and Wilmington metropolitan areas showing the log of NO_x emission rate calculated from the SMOKE model. For clarity, grid cells with emissions lower than 316 ton y^{-1} (log = 2.5) are left blank. Emissions are given on a 4 by 4 km UTM grid, necessitating a map projection different than the rectilinear lat-lon projection used for other figures. Three of the 4 monitoring stations with peak O_3 greater than 150 ppb are identified by circles with X's. Superimposed over the emission grid is the ground track for the G-1 aircraft for the afternoon flight of July 31, 1999. Numbers 1-7 identify grid cells with high NO_x emissions, described in Table 2.

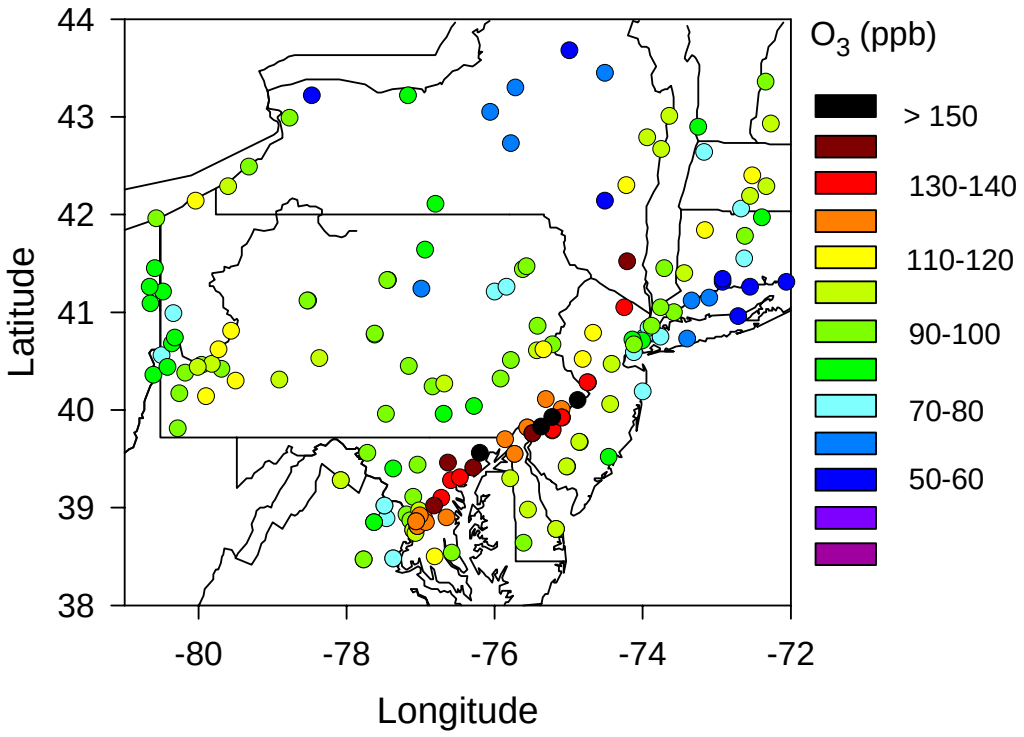

Figure 3. Maximum 1 hour average O_3 concentration observed at surface monitoring sites on July 31, 1999.

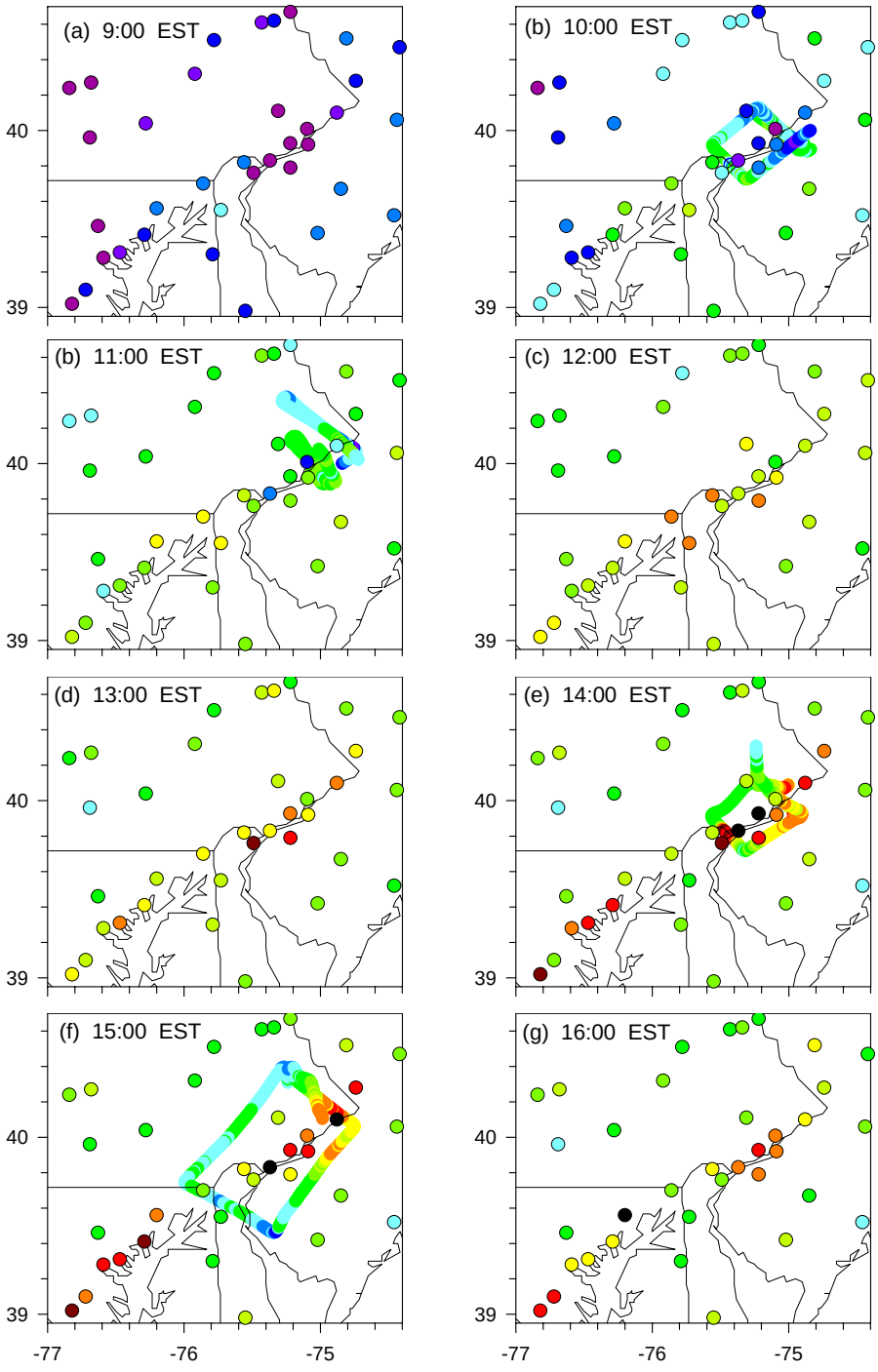

Figure 4. Surface O_3 from monitoring network and O_3 observed from G-1 on July 31, 1999. Color scale for O_3 concentration is given in Fig. 3. Eight panels each show 1 hour of data, from 9:00 to 16:00 EST. G-1 data is presented for the preceding 1 hour period. The surface data is a 1 hour average; e.g. panel (a) labeled 9:00 EST shows an average O_3 concentration for 8:00 – 9:00. The morning flight occurred between 8:53 – 10:58 EST; the afternoon flight between 12:54 – 15:01 EST. All of the G-1 observations are at an altitude below 1000 m.

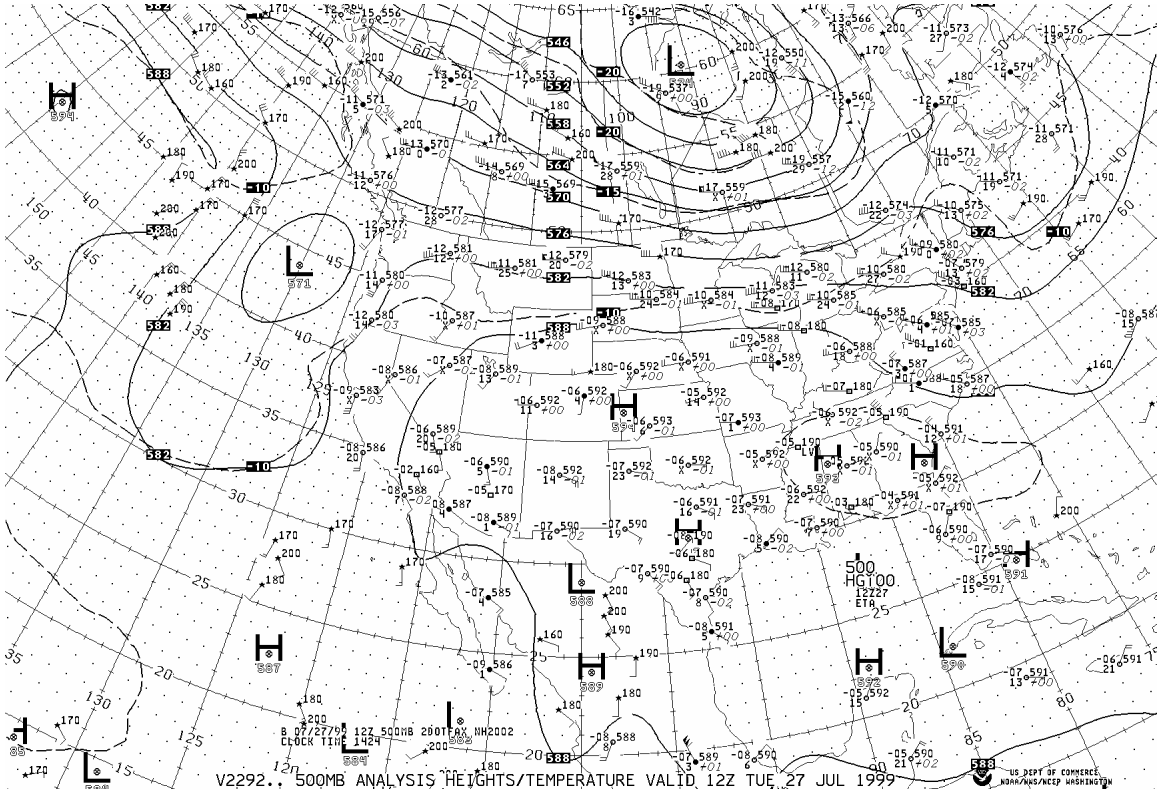

Figure 5. NCEP 500 mb analysis for 1200 UTC (7:00 EST) on July 27, 1999. Solid contours are geopotential height (in dm) and dashed contours are temperature (in Celsius). Station data is plotted using standard conventions.

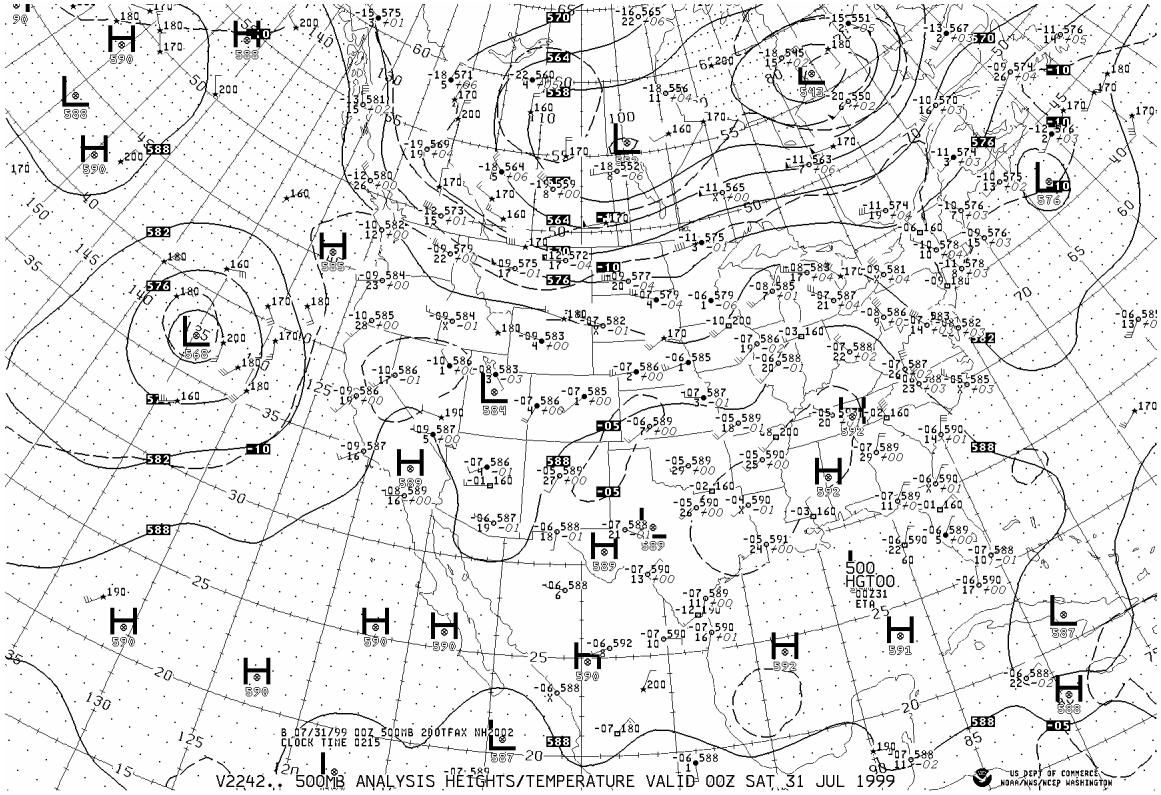

Figure 6. NCEP 500 mb analysis for 0000 UTC on July 31, 1999 (19:00 EST, July 30). Same format as Fig. 5.

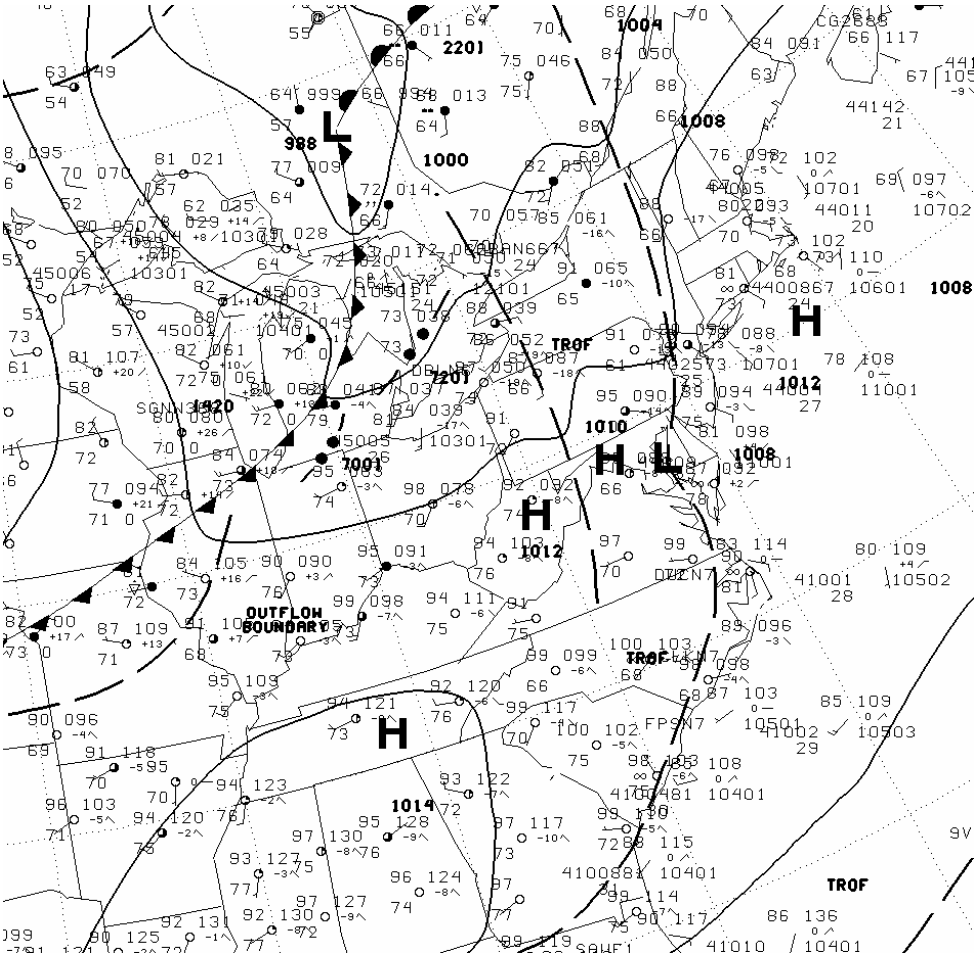

Figure 7. NCEP surface analysis for 1800 UTC (13:00 EST) on July 31, 1999.

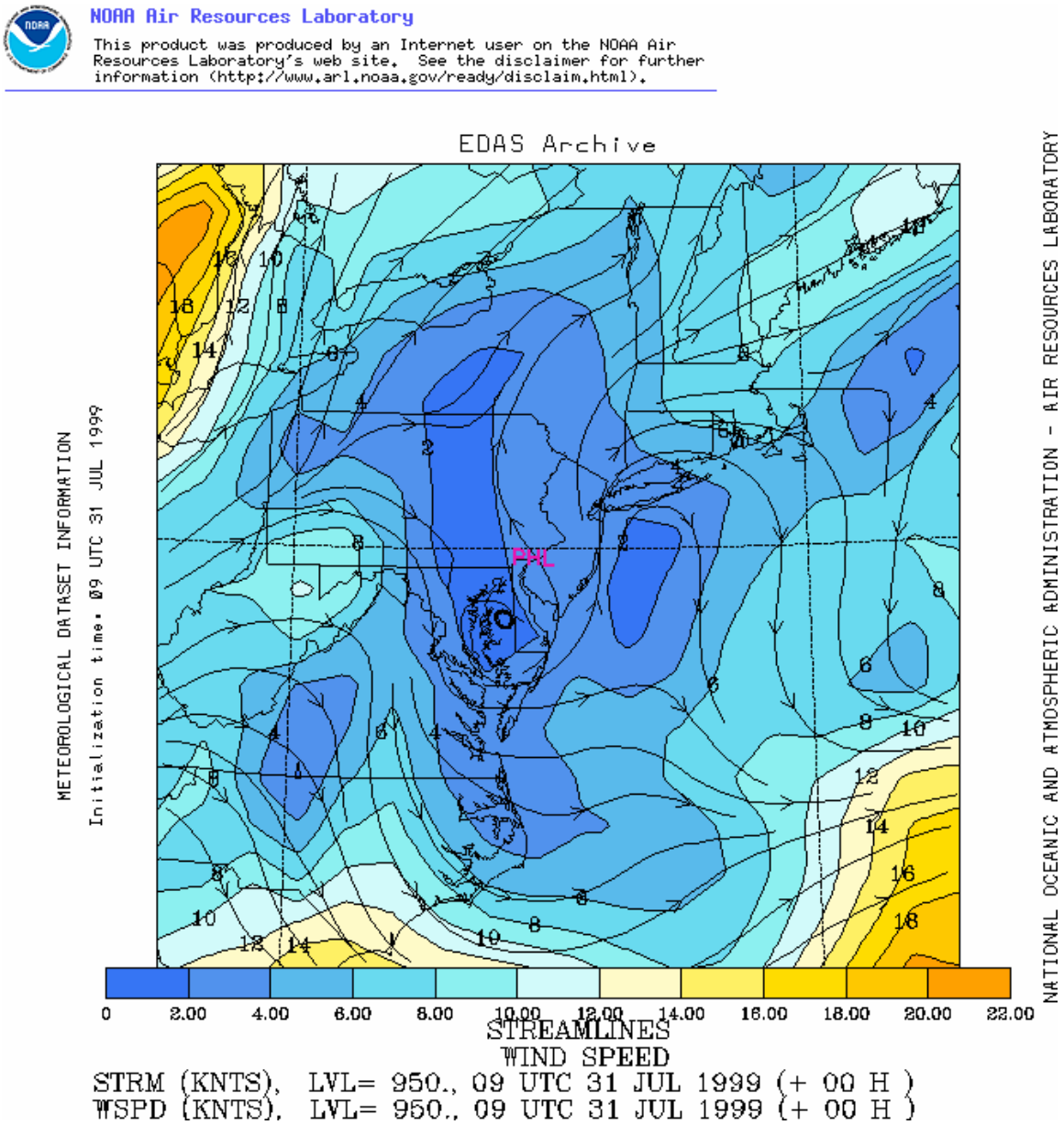

Figure 8. EDAS (Eta Data Assimilation System) winds at 950 mb at 9UTC (4:00EST) , July 31, 1999. Lines with arrows are streamlines. Wind speed given by color scale. Low pressure center indicated by closed circle, SSE of Philadelphia. Graphic produced by NOAA Air Resources Laboratory.

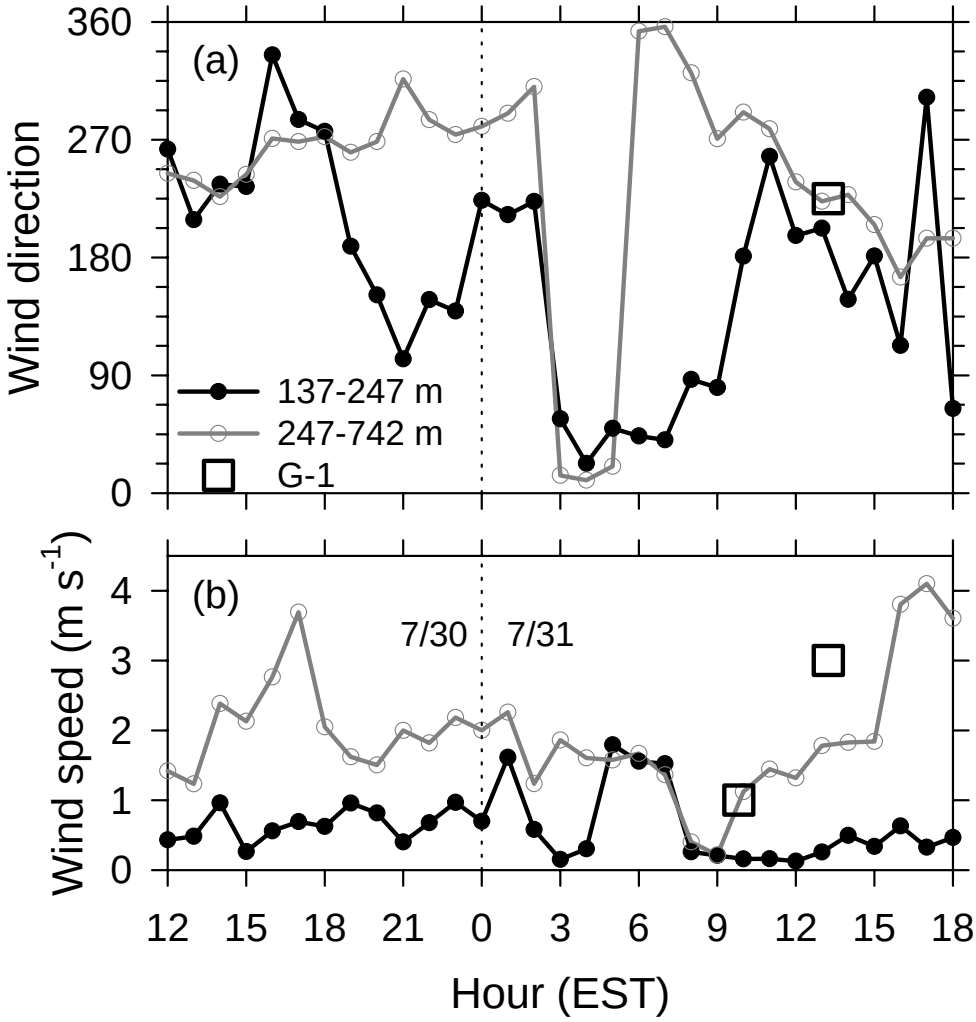

Figure 9. Boundary layer winds from the Baxter RASS on July 30 and 31, 1999. (a) direction, (b) speed. Winds are vector average values over the altitude interval 137-247 m or 247-742 m, as indicated. Winds from the G-1 are at an altitude of ~ 500 m, at the location of the Delaware plume. Wind direction from the morning G-1 flight was highly variable due to low wind speed.

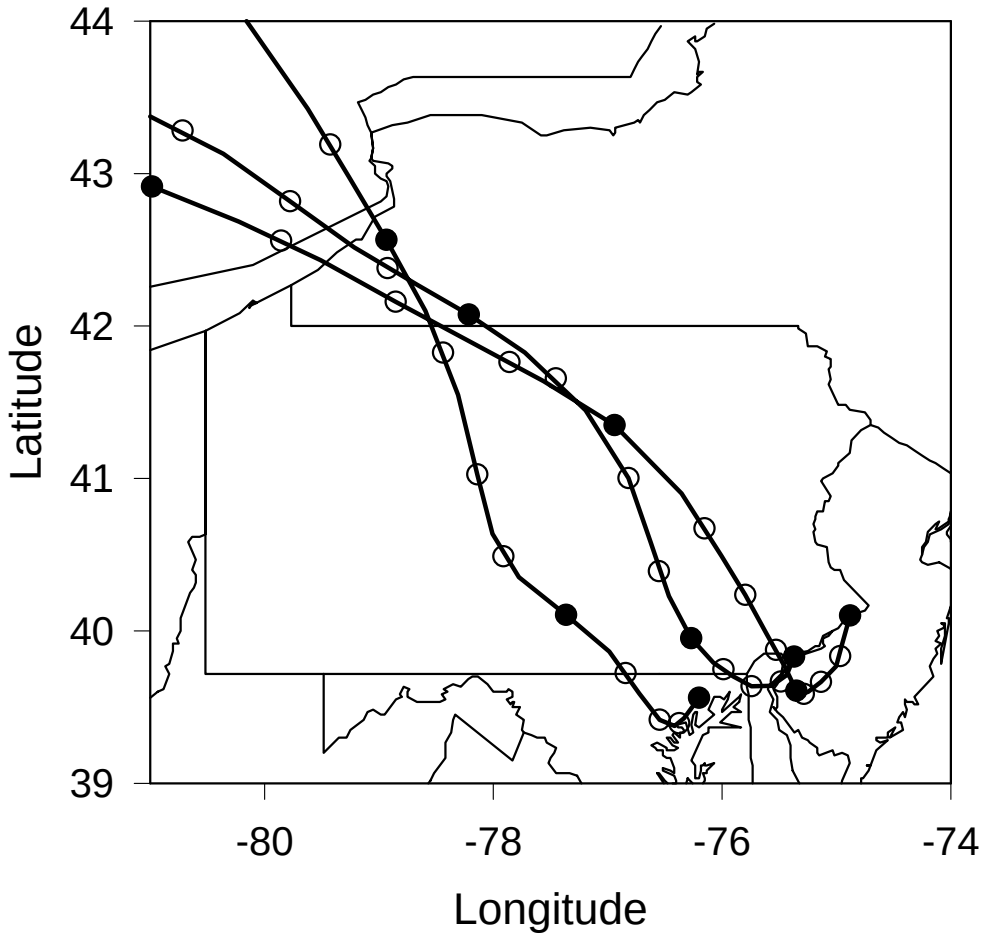

Figure 10. Back trajectories from the Hysplit model, calculated using EDAS meteorological data. Trajectories terminate at an altitude of 1000 m at 3 of the 4 surface sites with peak O_3 concentration above 150 ppb on July 31, 1999. Termination times coincide with the peaks in O_3 concentration. From southwest to northeast the surface sites are Aldino, MD (16:00 EST); Chester, PA (14:00 EST); and Bristol, PA (15:00 EST). Trajectory for Elmwood Street in Philadelphia omitted for clarity. Open symbols placed at 3 h intervals, filled-in circles at 12 h intervals.

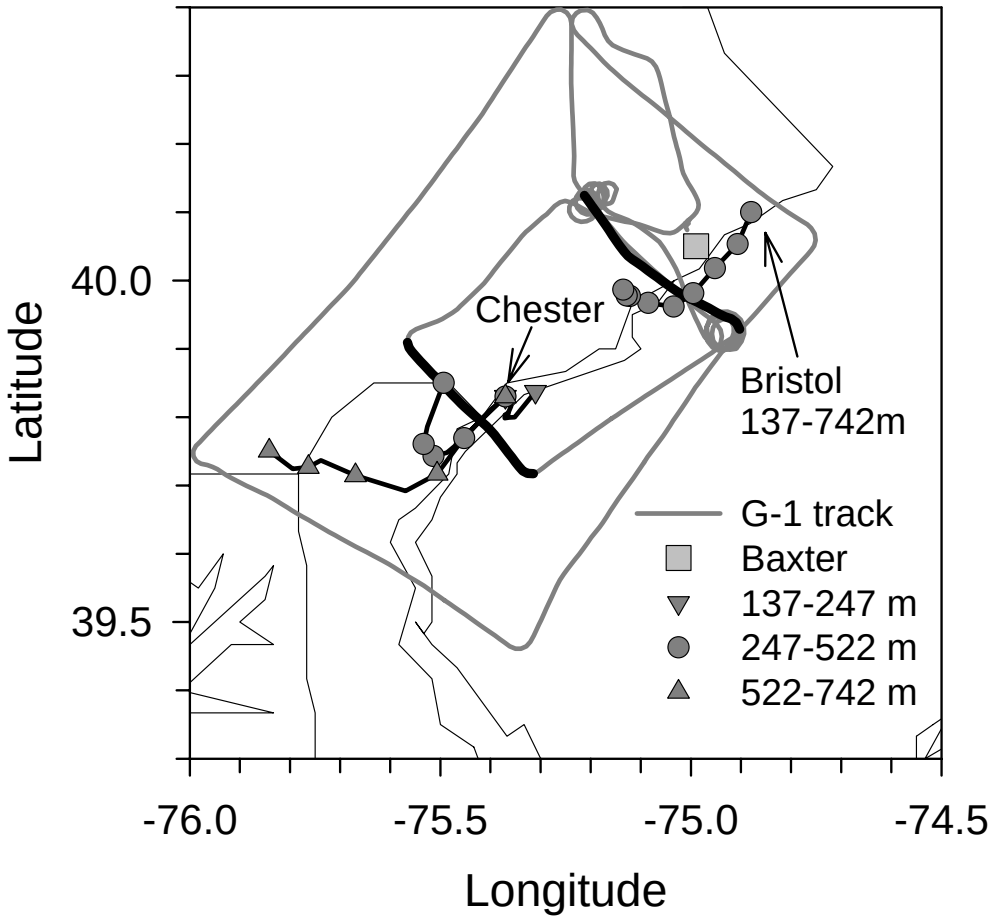

Figure 11. Back trajectories calculated from layer averaged winds measured at the Baxter RASS site. Trajectories terminate at 2 high O_3 surface monitoring sites; Chester, PA and Bristol, PA at 14:00 and 15:00 EST, respectively. Depth of averaging layer given in legend. G-1 ground track is for the July 31 pm flight. Segments that cross the Delaware plume and North Philadelphia plume are indicated in bold. Data from these segments are presented in Figs. 14 and 15. Data from the July 31 am flight presented in Fig. 13 includes a segment from the west side of the box in addition to the south side used for the afternoon graph.

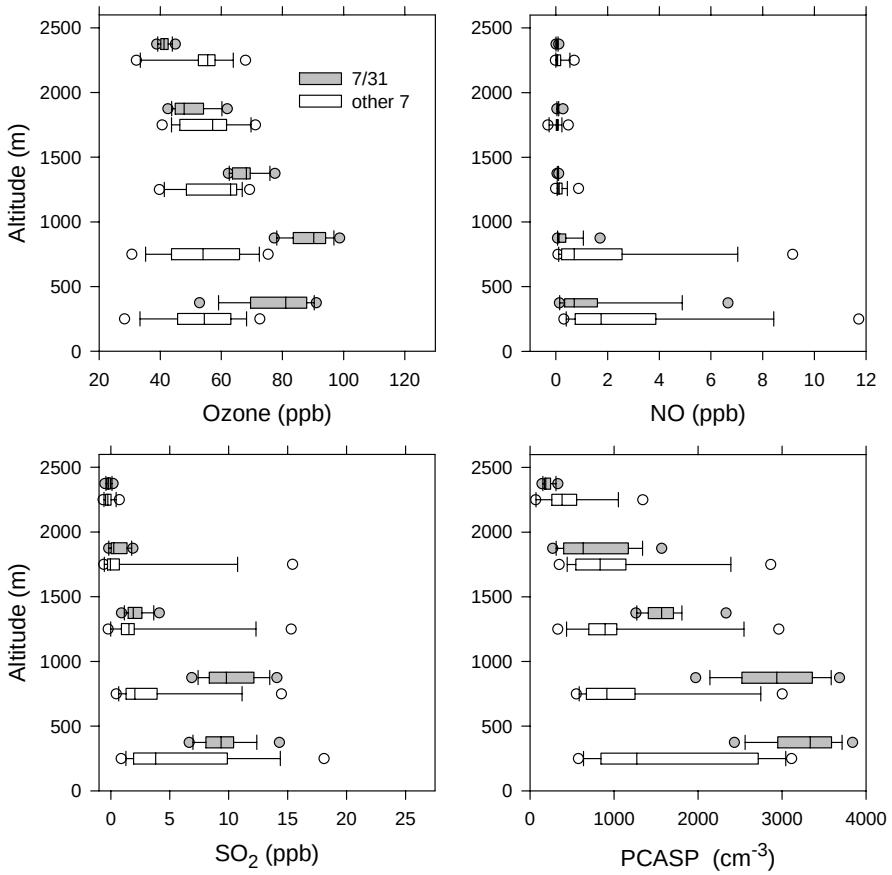

Figure 12. Frequency distribution of (a) O_3, (b) NO, (c) SO_2, (d) accumulation mode aerosol (PCASP) as a function of altitude. Data are from those portions of 8 morning aircraft flights located in the rectangular area designated as "urban box" in Fig.1. Data are grouped into 500 m bins between 0 and 2500m (i.e., 0-500 m, 500-1000 m, etc). The July 31 data are offset for clarity. Observations at an altitude above 500m have been screened using the standard deviation of potential temperature as a surrogate measure of turbulence intensity to remove boundary layer data points [*Berkowitz and Shaw*, 1997]. Central portion of bar indicates 25th, median, and 75th percentile values. Caps are 10 and 90th percentile values. Circles are 5th and 95th percentile values.

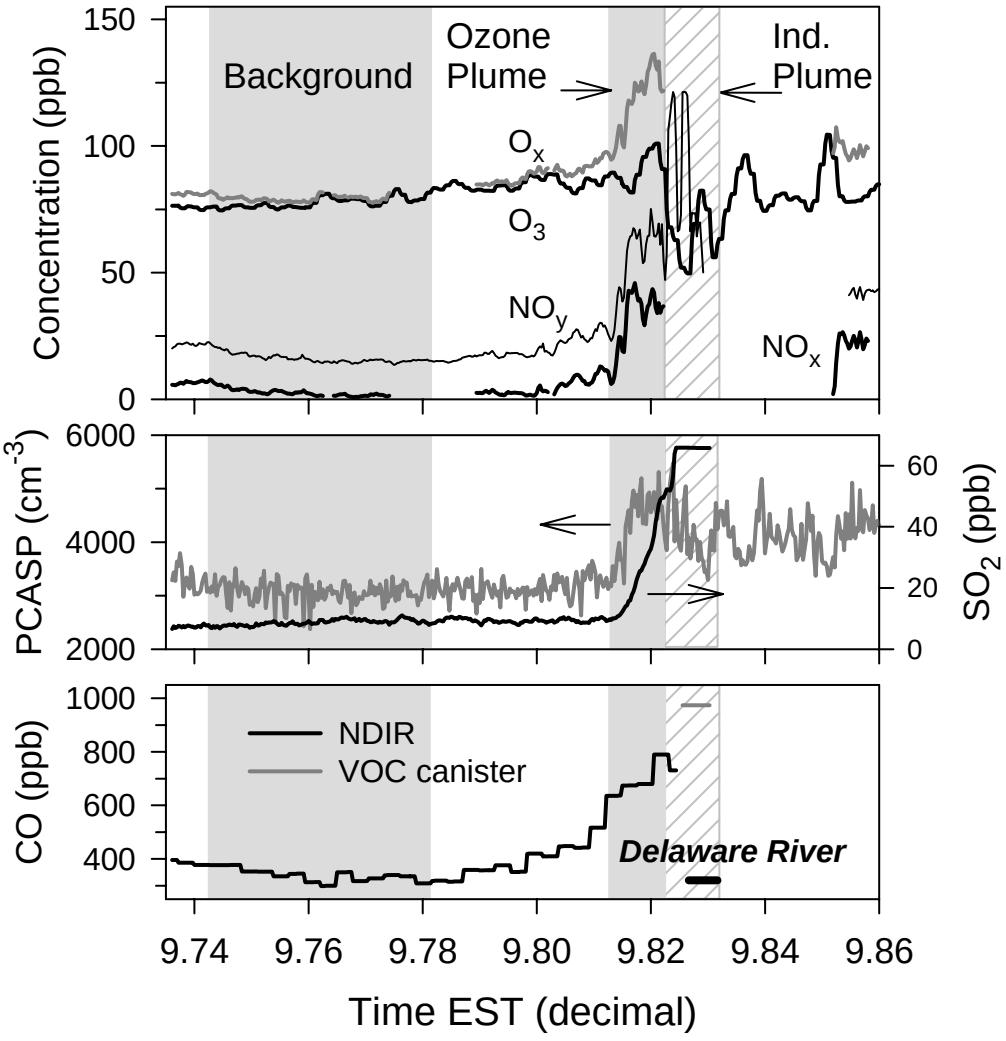

Figure 13. Chemical measurements from the July 31 G-1 morning flight versus time for a segment that includes the Delaware plume at 440 m altitude. Geographic region on south side of flight track highlighted in Fig. 11 extends from decimal time 9.78 to 9.86. Location of Delaware River noted. A background region and the "O_3" plume referred to in the text and Table 4, are shown as shaded areas. An "Industrial" plume caused by emissions near the Delaware River almost underneath the G-1 ground track is indicated by a cross-hatch. The forward edge of the Industrial plume occurs in a region with missing data and cannot be precisely defined. (a) O_x, O_3, NO_x, NO_y. Calculated NO_2 is not reliable in the extremely high concentration region, cross-hatched, area and therefore O_x and NO_x are not given. (b) SO_2, PCASP, (c) CO from continuous NDIR and from canister sample. Trace gas and aerosol observations are presented at 1Hz except for NDIR CO which is presented at 0.1 Hz and canister CO which is from a 17 s whole air sample.

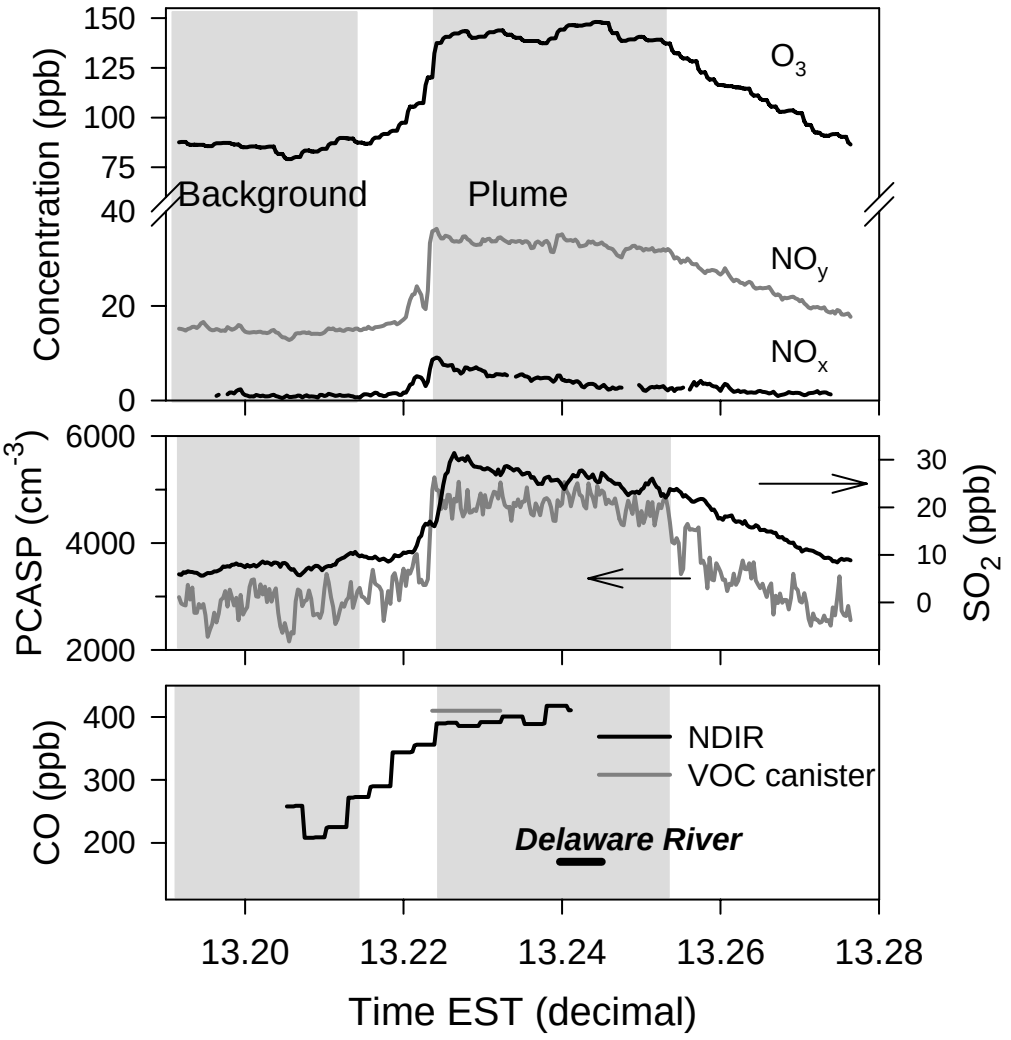

Figure 14. Chemical measurements from the July 31 G-1 afternoon flight versus time for a segment that includes the Delaware plume. Geographic region is shown in Fig. 11. Location of Delaware River noted. Plume and background regions used in Table 4 are shown as shaded areas (a) O_3, NO_x, NO_y (b) SO_2, PCASP, (c) CO from continuous NDIR and from canister sample. Trace gas and aerosol observations are presented at 1 Hz except for NDIR CO which is presented at 0.1 Hz and canister CO which is from a 31 s whole air sample.

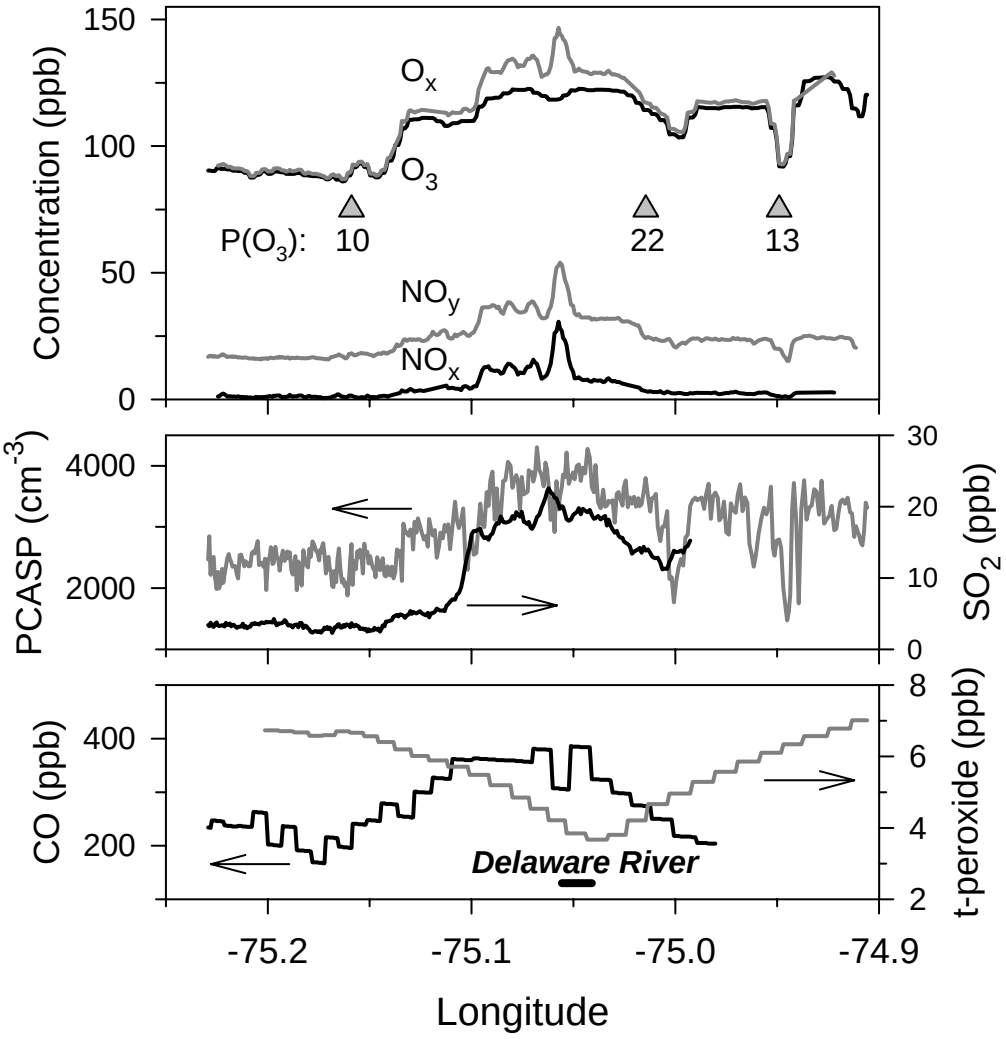

Figure 15. Trace gas and aerosol concentrations measured at 870 m altitude on a transect of the North Philadelphia plume between 13:51 and 13:57 EST. Location of Delaware River noted. Triangles in top panel show locations of VOC samples. $P(O_3)$ calculated at those locations has units of ppb h^{-1}.

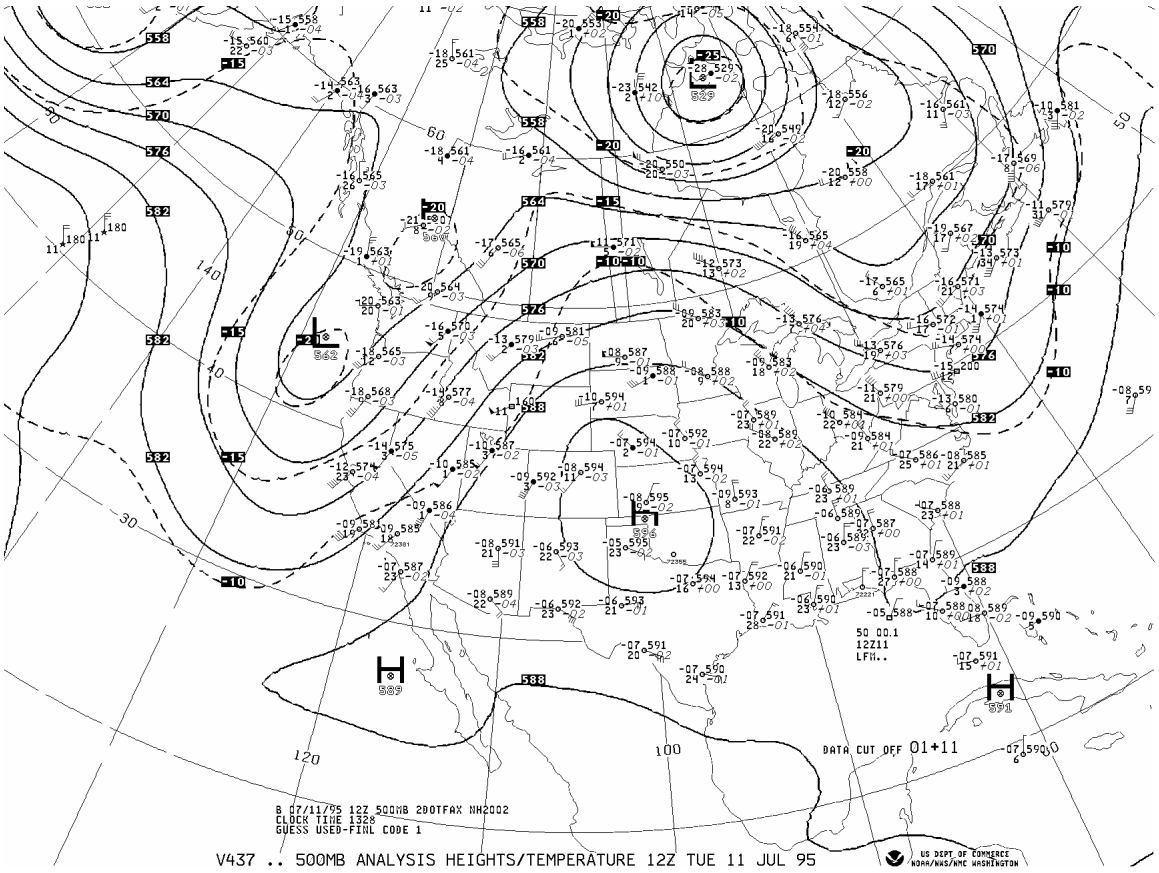

Figure 16. NCEP 500 mb analysis for 1200 UTC (7:00 EST) on July 11, 1995. Same format as Fig. 5.

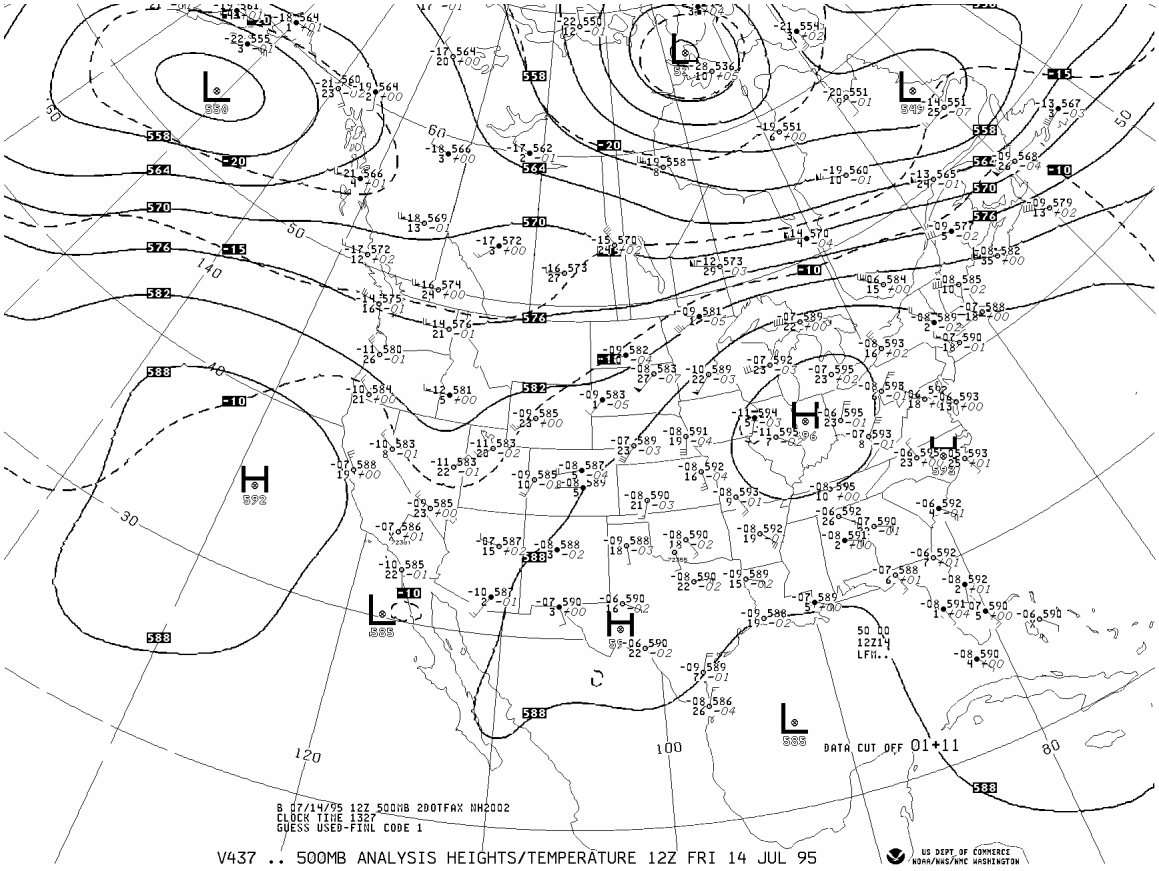

Figure 17. NCEP 500 mb analysis for 1200 UTC (7:00 EST) on July 14, 1995. Same format as Fig. 5.